

Insulating Biomaterials N01-NS-2-2347

Fourteenth Quarterly Progress Report January-March, 2006

National Institutes of Health

National Institute of Neurological Disorders and Stroke

Neural Prosthesis Program



InnerSea Technology

**1 DeAngelo Drive
Bedford, MA 01730**

Contributors:

Dave Edell, PI

Robyn Edell, Testing

Sean Sexton, Instrumentation and Software

Ying-Ping Liu, Assembly and Testing

Karen Gleason, Chem Eng (MIT)

Shannan O'Shaughnessy, Grad Student, Chem Eng (MIT)



The goal of the Insulating Biomaterials work is to identify and evaluate materials, coatings, and assembly techniques suitable for protection of integrated circuit devices being considered for neural prosthetic applications.

Final Report Outline

The Final Insulating Biomaterials Report due in October, 2006 is being formulated and an initial outline is below.

1. Introduction to common issues associated with implantable electronic devices that may be solved by understanding Insulating Biomaterials.
2. Initial choices for materials that can be considered for implantable electronic devices.
 - a. General guidelines
 - b. Insulators
 - c. Conductors
 - d. Substrates
 - e. Components
3. Instrumentation and devices for testing of candidate Insulating Biomaterials.
 - a. Thermal accelerated testing.
 - b. Mechanical accelerated testing.
 - c. Chemical accelerated testing.
 - d. Accelerated detection.
 - e. In-Vivo testing.
4. Important classes of Insulating Biomaterials
 - a. Ceramics
 - b. Polymers
 - i. Silicon based



ii. Carbon based

5. Tabulation of materials tested under the Insulating Biomaterials Contract and status of long term testing.
6. CVD
7. Legal issues with use of commercially available materials.

Instrumentation Systems

Accelerated detection of degradation is the most reliable tool for studying materials for implantable devices. The new Passivation Test System consists of 4 major components: the Tube Top, the Measurement Unit, the Data collection Unit, and the Calibration Unit. These components are described below. Basically, as illustrated in Figure 1 the device to be tested is placed into the saline soak tube.

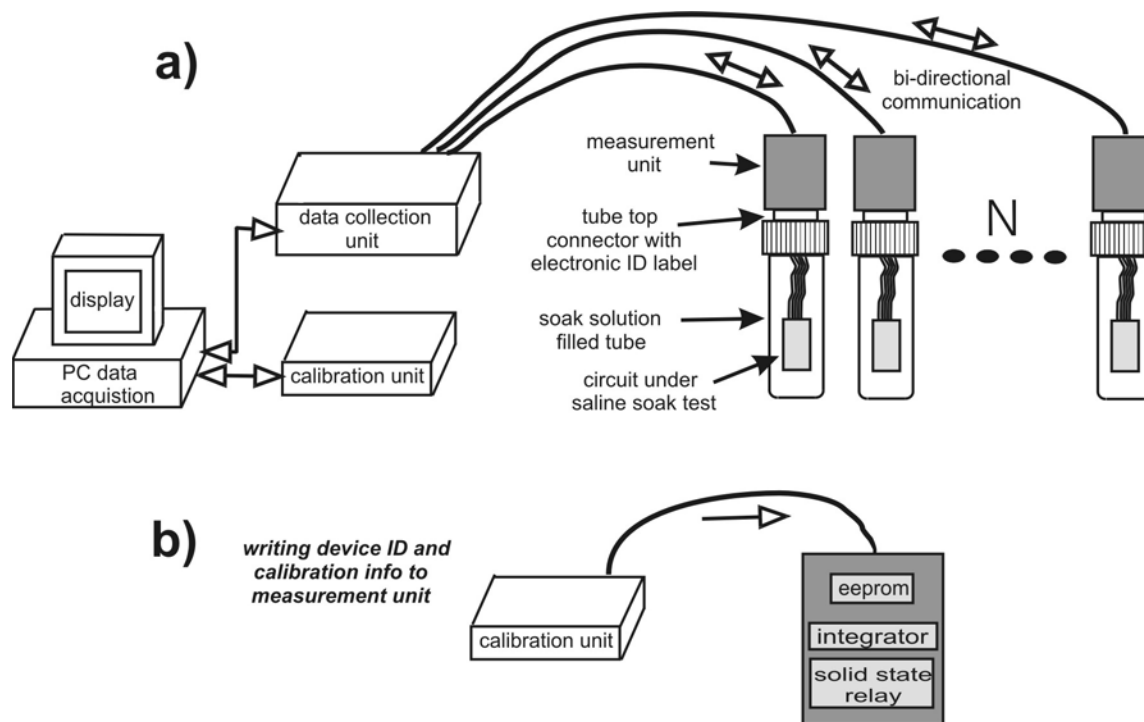


Figure 1: Cartoon showing basic elements of new test system.

1) Tube Top - This provides: a physical attachment point for the device under test; the electrical connections to the system; and an EEPROM that contains information about the particular device in that is under soak test in that respective tube.



- 2) Measurement Unit - This contains: the analog circuitry required to perform the measurement; a calibration check unit; a continuity tester for triple track devices; and another EEPROM which contains required calibration information.
- 3) Data Collection Unit - This accepts the data (consisting of timing signals) from the measurement units, converts them into leakage values, and transmits those values to a host computer.
- 4) Calibration Unit - This is a standalone unit that is used with each device before any testing at all is performed, and it is normally used only at the onset of testing. Thus, if a device is tested each day for 100 days, the Calibration Unit is “hooked” up to Measurement Unit at the start of day 1 so that device identification data can be downloaded to the EEPROM that is located on the Tube Top, along with the calibration information particular to the device under test and that will be needed for the Measurement Unit to interpret the measured parameters for every succeeding test day.



Recent Results:

Fabrication of the system's hardware was contracted to Lightspeed Manufacturing of Methuen, Massachusetts. Lightspeed assembled 5 Data Collection units, and 16 hot swap controllers, saving InnerSea a large amount of manufacturing time. One system has been fully assembled (see above) and is in the process of performance testing. No more problems have been found in either the hardware or the firmware of the system.

The software development is 75% complete, with all of the major components functioning. The software is being developed using Microsoft Visual Basic .Net, in



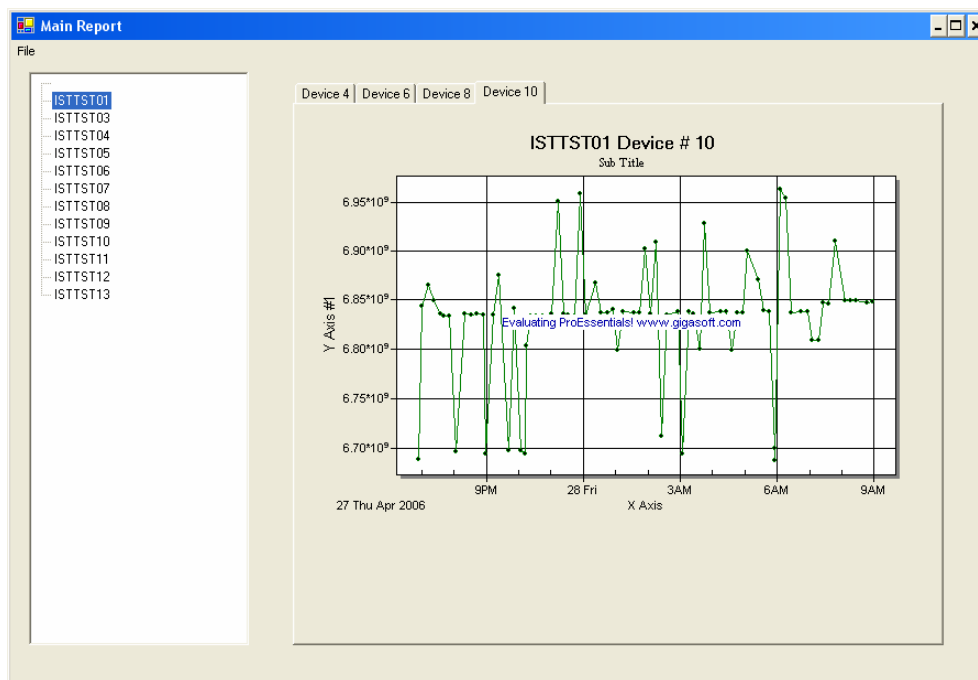
conjunction with the MySQL database system. When the software is run, it polls the network on port 2525 (a generally unused port) to see if there are any Data Collection Units connected. If one or more are found, then the software interrogates each, to discover what test jars are connected. Any changes in configuration are noted in the database system.



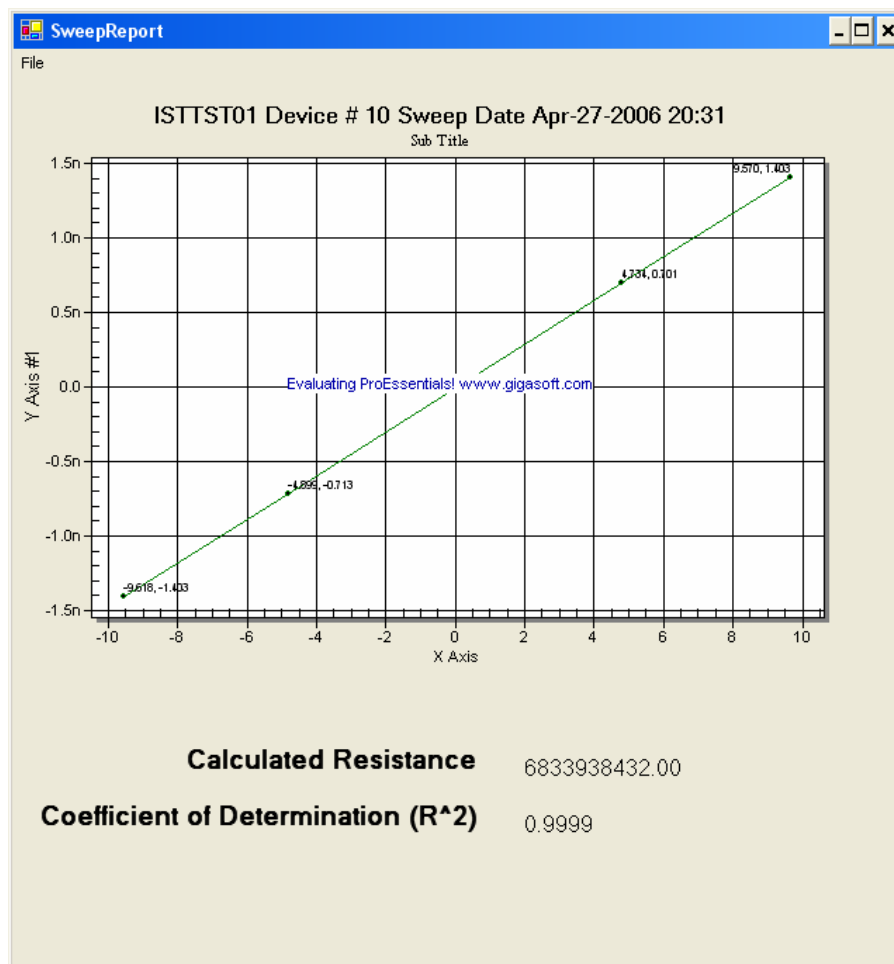
The above screenshot shows the main screen of the software. The item in red represents the detected data collection unit. The items shown in blue represent the individual jars connected to the system. The items shown in purple represent the



individual test devices. When the system is started, the data collection unit's ID changes from red to green to indicate the system is running. To view the results the user selects the Reporter option from the tools menu



The resistance results for the selected device are shown in a graphical form as above. You can see by the displayed data that the system error is better than 5%. Each point on this graph is calculated by a linear fit of the measured leakage currents at the each of the sweeps bias points. Clicking on a point reveals the details of the sweep.



As seen above, the sweep results are displayed graphically as were the long term results. Each of the bias points is displayed with its corresponding current result. A linear regression is applied to this data. The offset coefficient is dropped, and the inverse of the slope coefficient is the resistance. We also show the R squared value of the fit.

Remaining Work to be Accomplished for Accelerated Detection System

Future Work

As noted in the previous section, the hardware and firmware portion of the design is complete. Now we are focused solely on completing the host software package. Some items that are in progress are:

1. Providing additional statistics to describe the quality of the measured data



2. Providing additional data export functionality
3. Cleaning up the user interface (i.e. correcting chart axis annotations)
4. Providing printing functionality for the report generator
5. Additional error detection/logging functions
6. Adding the ability for the user to add comments, pictures, and keywords to the device database.
7. Reducing program overhead through more efficient use of multithreading
8. Providing a concise method of determining partial sweeps, and exclude this data from the final dataset
9. System hardware and software documentation

InterDigitated Electrode Testing In-Vitro

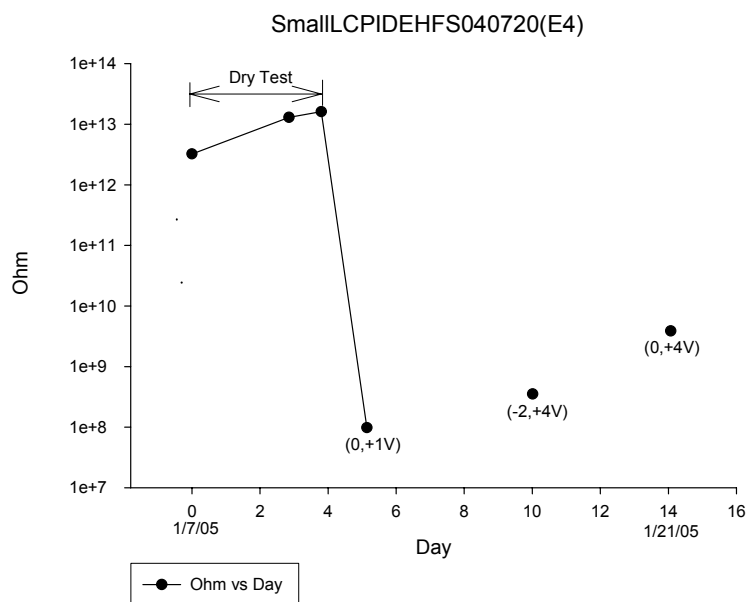
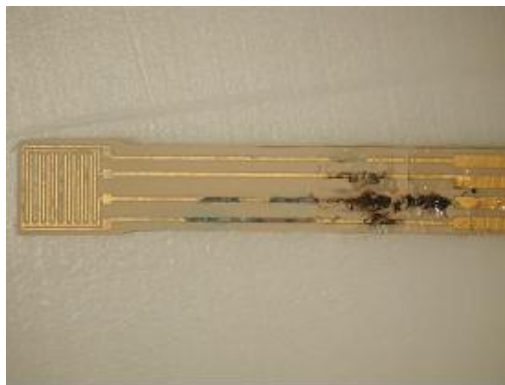
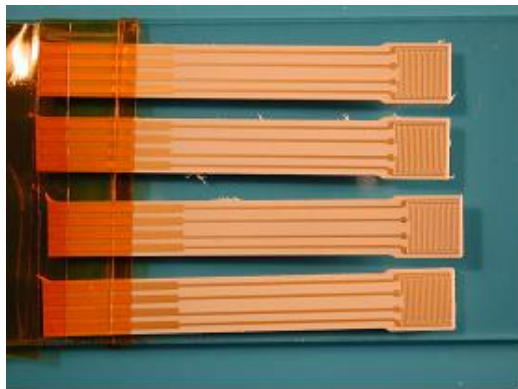
LCP and Quartz IDEs coated with CVD Silicone: Three sets of inter digital electrodes (SmallLCPIDEHFS040720, LongLCPIDEHFS040720, QuartzIDEHFS040720) coated with hot filament deposited silicone from MIT were examined. Depositions were performed using V_3D_3 + tertbutyl peroxide ($P=300\text{mTorr}$, $T_f=500^\circ\text{C}$, $T_s=60^\circ\text{C}$) to a thickness of $\sim 5\mu\text{m}$ as measured on a reference Si wafer piece coated concurrently. Each device was glued on a microscope slide which was then inserted through a precut slot on a test jar's cap and was fixed with quick cure silicone. The contacts were outside to avoid the failures observed around the solder joints due to solder flux contamination. The experiment results up to 8/12/05 are summarized as follows.

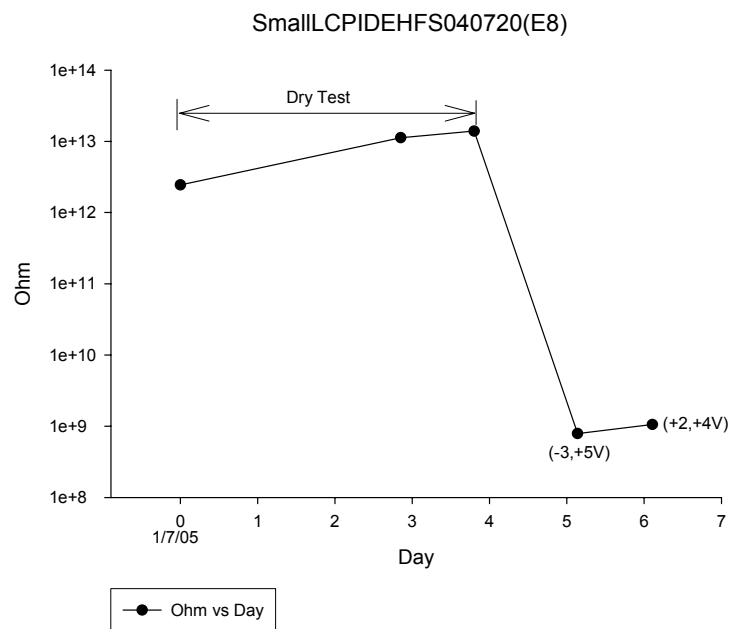
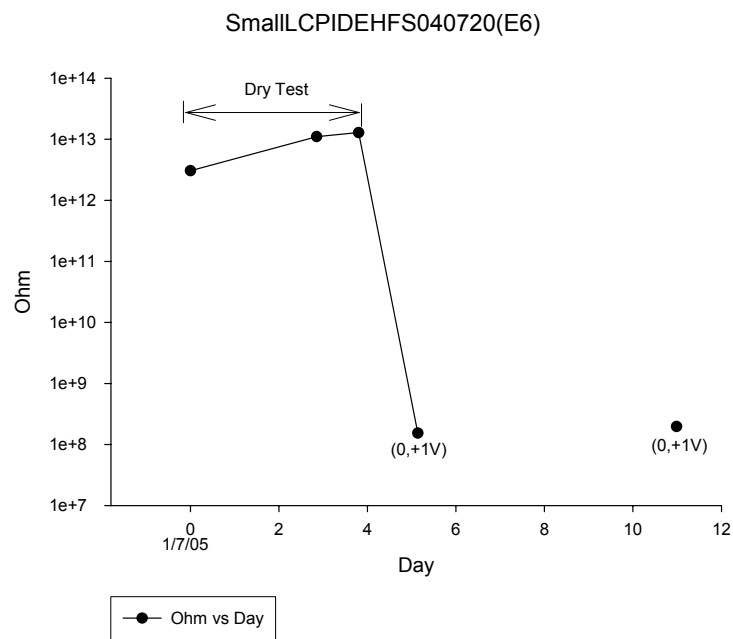
SmallLCPIDEHFS040720

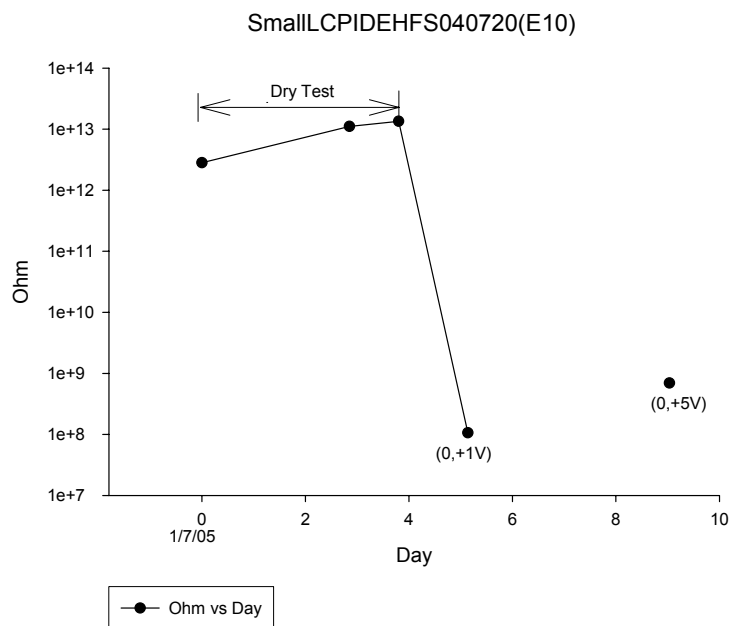
Four small LCP IDEs coated with CVD silicone (see below) were assembled into a test jar. The devices were initially tested without solution (dry test). In a five-day measurement, the devices had resistance at 10^{12} to $10^{13}\Omega$. However, after the test jar was filled with Phosphate Buffered Ringer (PBR) on 1/12/05, all the devices were failed within the first two measurements. The pass test was terminated on 1/24/05 and the resist data are summarized in Table1. Microscopic study showed that for all the devices,



extensive corrosion was found on the leads especially at the region where the samples were fixed to the cap by quick cure silicone (MED2-4220). Perhaps there was physical tension from silicone MED2-4220 which weakened the CVD silicone coatings on the substrates, particularly over the metallization where there would be little adhesion. While extensive corrosion was also found on the IDEs for device E08, no corrosion or minimum corrosion was observed on the IDEs for E04, E06, and E10 respectively.

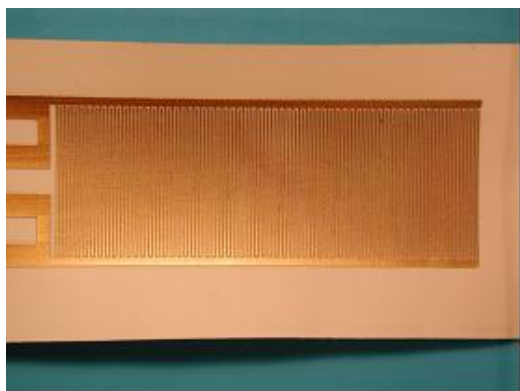


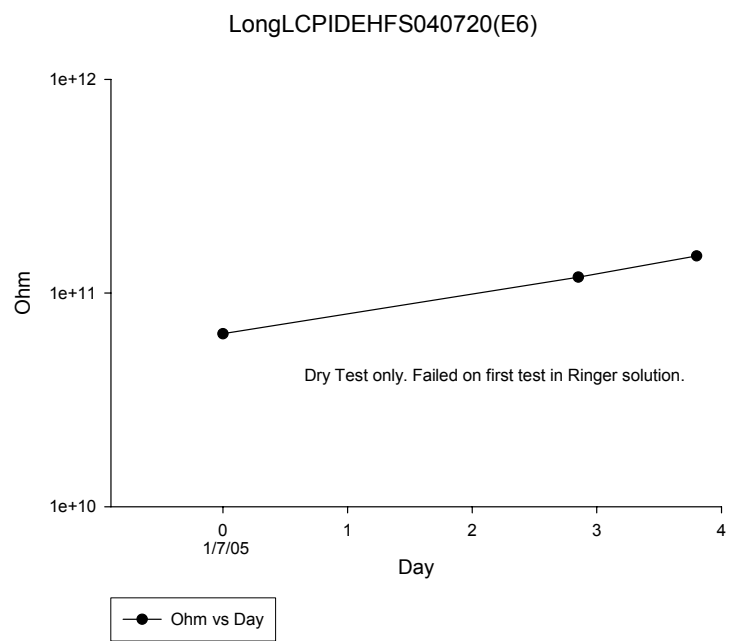
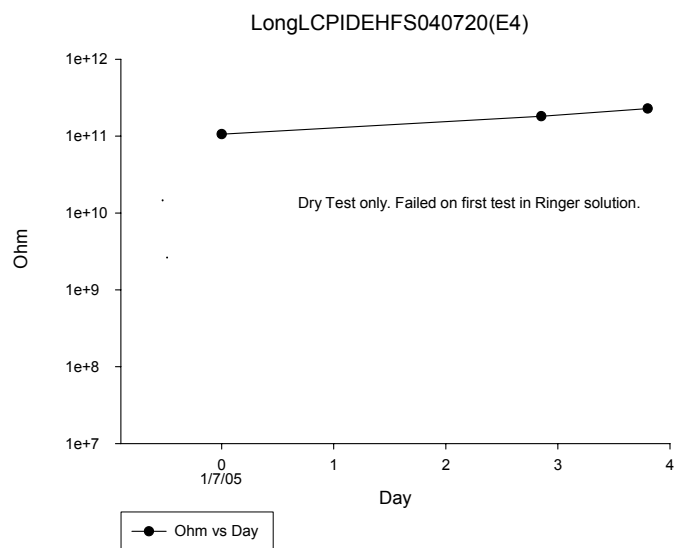


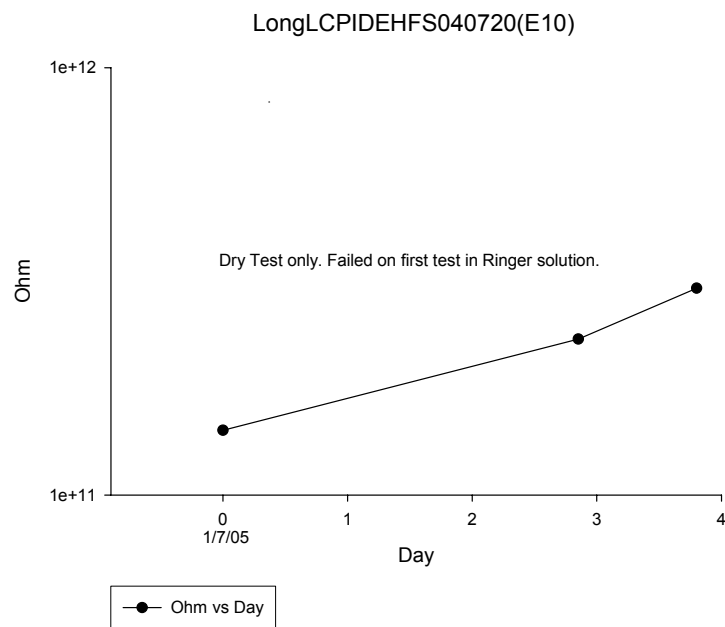
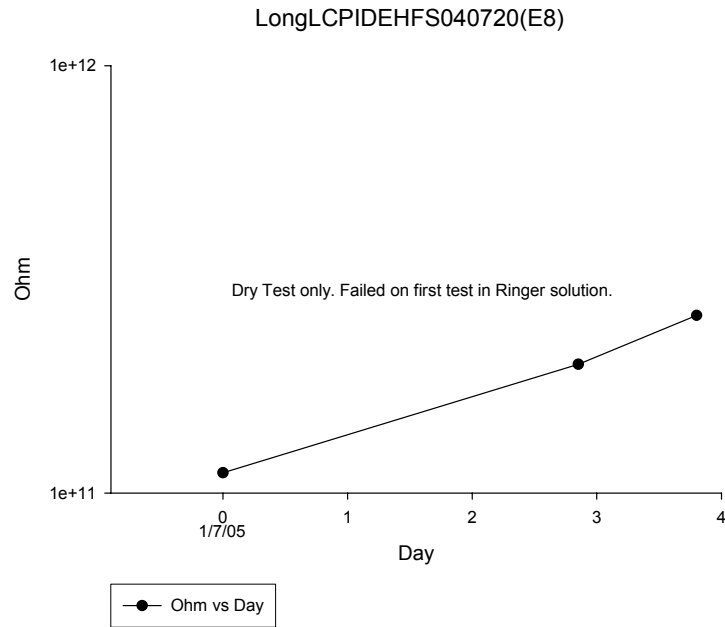


LongLCPIDEHFS040720

Four long LCP IDEs coated with CVD silicones were cut short and assembled into a test jar as outlined above. A five-day dry test showed the devices had the resistance of $10^{11} \Omega$. After the test jar was filled with Phosphate Buffered Ringer (PBR) on 1/12/05, all the devices were over ranged on the first measurement. The pass test was terminated on 1/24/05 and the resist data are summarized in Table2. Microscopic study showed green bluish copper corrosion products all over the triple tracks for all four devices.





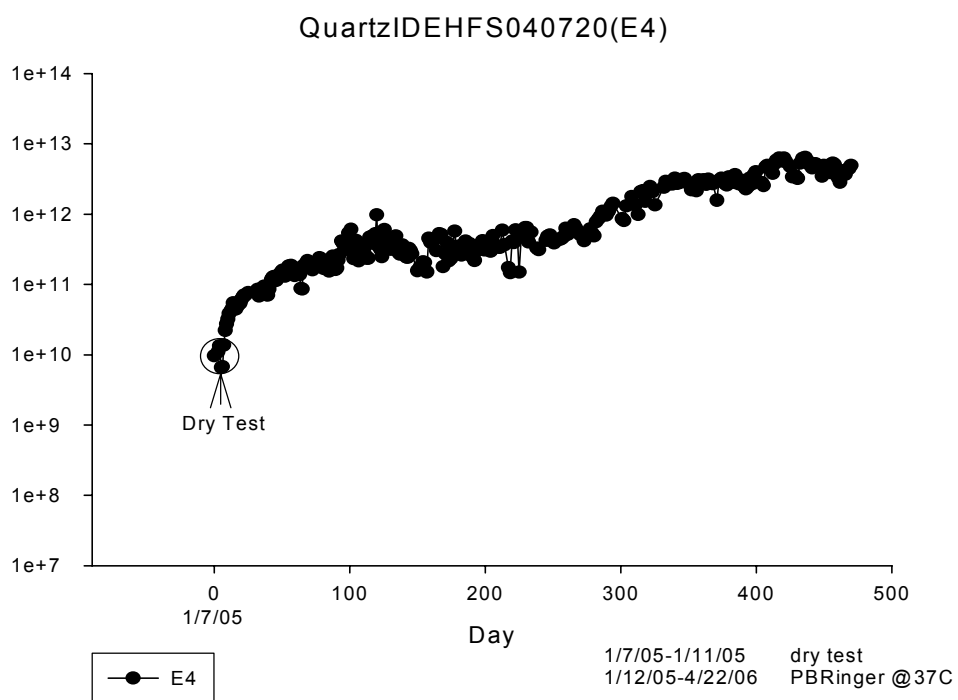
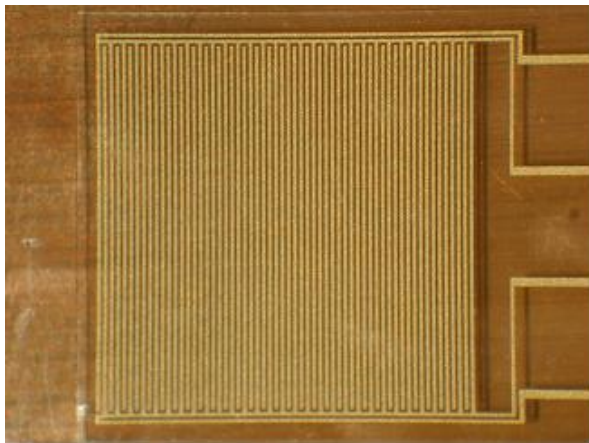


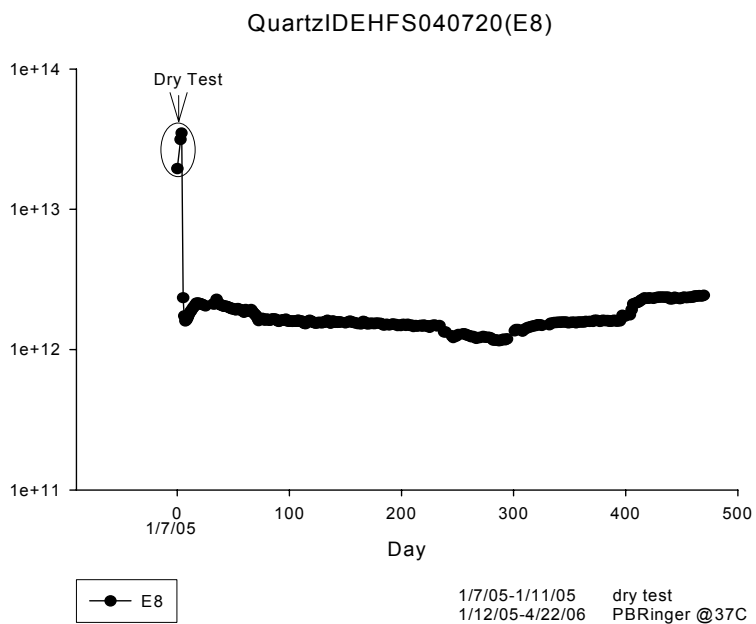
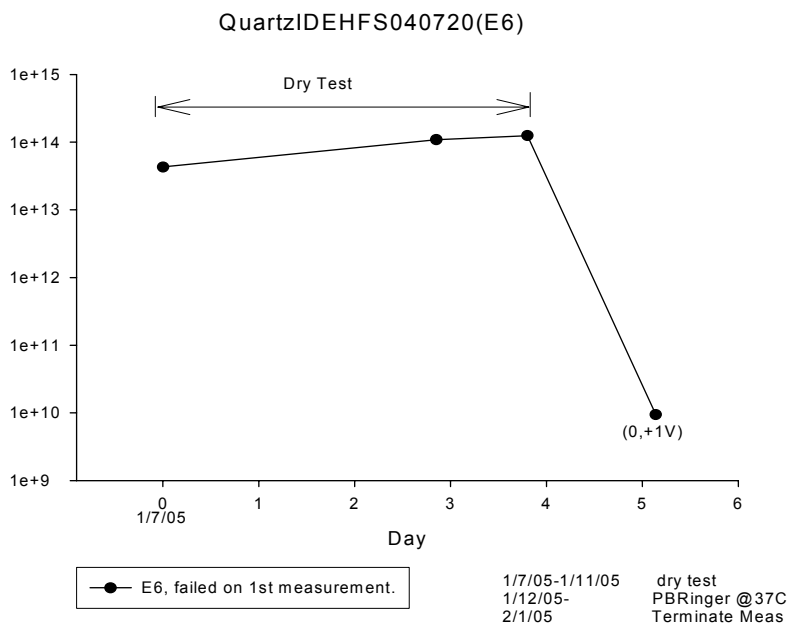
QuartzIDEHFS040720

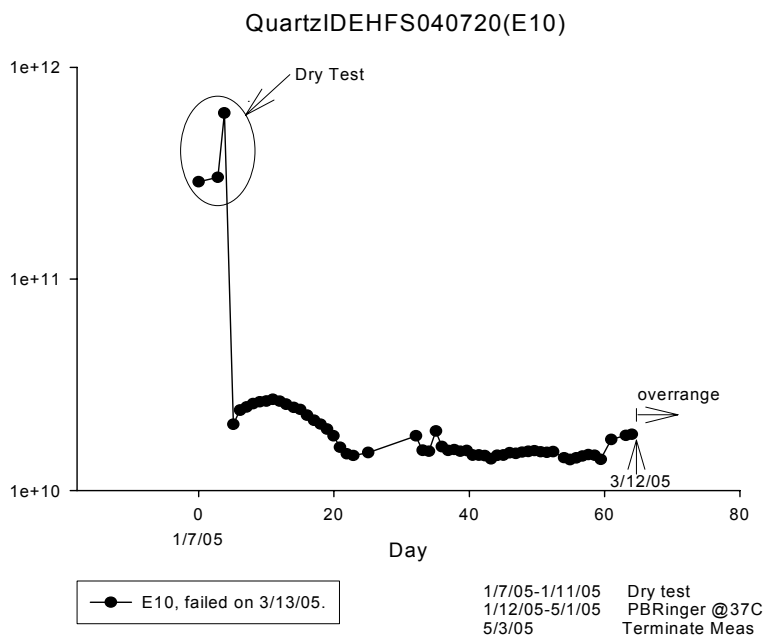
Four quartz IDEs coated with CVD silicone were assembled into a test jar. Dry test showed the devices E4 & E10 had resistance of 10^{10} and $10^{11} \Omega$ respectively, and E6 & E8 at $10^{13} \Omega$. After the test jar was filled with Phosphate Buffered Ringer (PBR) on 1/12/05, E6 failed on the first wet test and the measurement was terminated on 2/1/05. During 15 months testing, the resistance of E4 has gradually increased from 6.6×10^9 to $4.9 \times 10^{12} \Omega$ and E8 remains at $10^{12} \Omega$. Device E10 continues at $10^{10} \Omega$ level for a period



of two months and then suddenly failed on 3/13/05. E10 was terminated on 5/3/05. Corrosion on IDE is observed on both E6 & E10. Tests for E4 and E8 are continuing.







LCP IDEs with Platinum Catalyzed Silica Filled Silicone or Epoxy Encapsulation

Three batches of LCP-IDE samples from Foster-Miller Corporation have been examined. The experiment results are summarized as follows.

LCPIDE010328

LCPIDE010328 is the first batch of LCPIDE samples from Foster-Miller under test. In this batch, Cu used for deposition is less flexible. Moreover, the Cu/Au traces between triple tracks (TT) and contact pads are thin and easy to break. Four triple track devices, two on thick LCP (LCPIDE010328B06 & LCPIDE010328B08) and two on thin LCP (LCPIDE010328C06 & LCPIDE010328C08), were assembled as shown in picture b_LCPIDE010328B06_OV. 5 mil Ag wires insulated with Teflon were connected onto contact pads with Ag epoxy H20E. The devices were then encapsulated with either epoxy EPO-TEK301 from EPOXY Technology or silicone MED4-4220 from Nusil Technology. For EPO-TEK301 encapsulated devices, LCPIDE010328B06 and LCPIDE010328C06, epoxy was cured at 65°C for 1 hour. For MED4-4220 encapsulated devices, LCPIDE010328B08 and LCPIDE010328C08, silicone was cured at 110°C and 65°C respectively for 3 hours. The reason for low temperature cure is to reduce thermal expansion, therefore to reduce the chances of breaking electrical continuity of the thin Cu/Au traces. However, at low temperature, silicone may not be fully cured. The



leakage measurements are made between TT itself as well as between TT and Pt reference electrode. All the Ag contacts were at outside of test tube. On 4/9/01, the devices were put under test at 37°C. The pass test results are summarized in Table 1.

From pass test results, it is observed that for EPO-TEK301 encapsulated devices, LCPIDE010328B06 and LCPIDE010328C06, resistance measured between TT in saline solution quickly dropped from 10^{11} to $10^8 / 10^9 \Omega$ after only few days test and then remained at $10^8 / 10^9 \Omega$. As for MED4-4220 encapsulated devices, LCPIDE010328B08 and LCPIDE010328C08, resistance began at the level of $10^8 / 10^9 \Omega$. In order to confirm the leakage pass is whether through the epoxy/silicone coatings or among the triple tracks themselves, two more experiments were conducted. In the first one, an adaptor was connected to the samples to make the leakage measurement between TT and Pt reference electrode in saline solution. The test lasted about one month and showed $10^8 / 10^9 \Omega$, the same resistance level as measured between TT for most of the time. In the second experiment, after rinsed with DIH₂O and baked at 70°C for 1 hour, the devices were put under dry test between TT for three and half months. As the devices became drier and drier with the time, the resistance mostly increased back to $10^{11} \Omega$, the same resistance level as initially shown in EPO-TEK301 encapsulated samples. On 10/17/01, the devices were once more put in saline solution. In 2nd wet test, all the resistances were again starting at $10^8 / 10^9 \Omega$. These experiments confirm that the leakage pass is indeed through the epoxy and silicone coating. EPO-TEK301 seems to protect triple tracks well initially, but apparently soon formed some micro cracks in the epoxy. Especially for LCP010328B06, even in the 1st wet test, the EPO-TEK301 encapsulated device was often swept at less than full range (-3V, +4V), an early indication of undertaking leakage process. The device failed completely after 1 month in 2nd wet test and microscopic exam showed more than half of the triple tracks was discolored from golden to brown (a_LCP010328B06_corrOV.jpg). A further exam revealed different types of corruptions such as dendrite (a2_LCP010328B06_DendrCorr_LMB42_DF40x), diffusion (a1_LCP010328B06_diffCorr_LM53-54_40x), and corrosion caused by poor silicone adhesion at the scratched area (a1_LCP010328B06_scratchCorr_M60_5x). The second EPO-TEK301 encapsulated device, LCP010328C06, lasted about 2.7 months in



2nd wet test before completely failure. There was no obvious color change on triple tracks in this device and corrosion at few local spots was caused scratch (a2_LCP010328C06_scratchCorr_R50-51_5x).

Although silicone has been used for encapsulating devices conventionally for a long time, the unsatisfactory performance of LCP010328C08 apparently is the result of under cure at low temperature. LCP010328C08, which was encapsulated with MED4-4220 cured at 65⁰C, quickly failed after 2nd wet test. A microscopic exam showed the device had a relative more extensive corrosion at the end of triple tracks (a2_LCP010328C08_corr_AMB1-B2_5x). Another silicone encapsulated device, LCP010328B08, which was cured at 110⁰C, showed much better hermetic protection. The device remained at 10⁸-10⁹ Ω for almost 5 months in 2nd wet test before failing and few small corrosion sites were found after testing. The corrosion apparently was caused by poor silicone adhesion at the contaminated locations and one typical example of this type corrosion, dendrite, was again observed on the triple tracks (a2_LCP010328B08_DendrCorr_LA13_DF40x).

Second Batch - LCP010921

LCP010921 is the second batch of LCPIDE samples from Foster-Miller with the improvements of wider Cu/Au leads and flexible Cu. Two sets of LCP010921 were encapsulated with either LCP or MED4-4220.

In the first set, four LCP010921A devices were covered with another layer of LCP and bonded with heat and pressure in a vacuum autoclave. Kester water-soluble solder was used to connect Belden 32AWG Teflon insulated wires to the contact pads. The solder flux was cleaned with DIH₂O/DIH₂O/Isopraponal (IPA), 1 min each in ultrasonic cleaner at 50⁰C. Solder joints were then coated with MED4-4220 silicone. Final assembly was similar to LCPIDE010328 and all the solder joints were outside of test tube. On 11/26/01, LCP010921A (E4, E6, E8, E10) began wet test in saline at 37⁰C. All four devices of LCP010921A were failed within the first 4-day test. Microscopic exam showed lots of defect such as pinhole, lint, and crack on LCP both front and back, which caused the leakage (e.g. a_LCP010921Ae08_lint2_5xEPIDFback, a_LCP010921Ae10_crack_40xEPIDFfront,

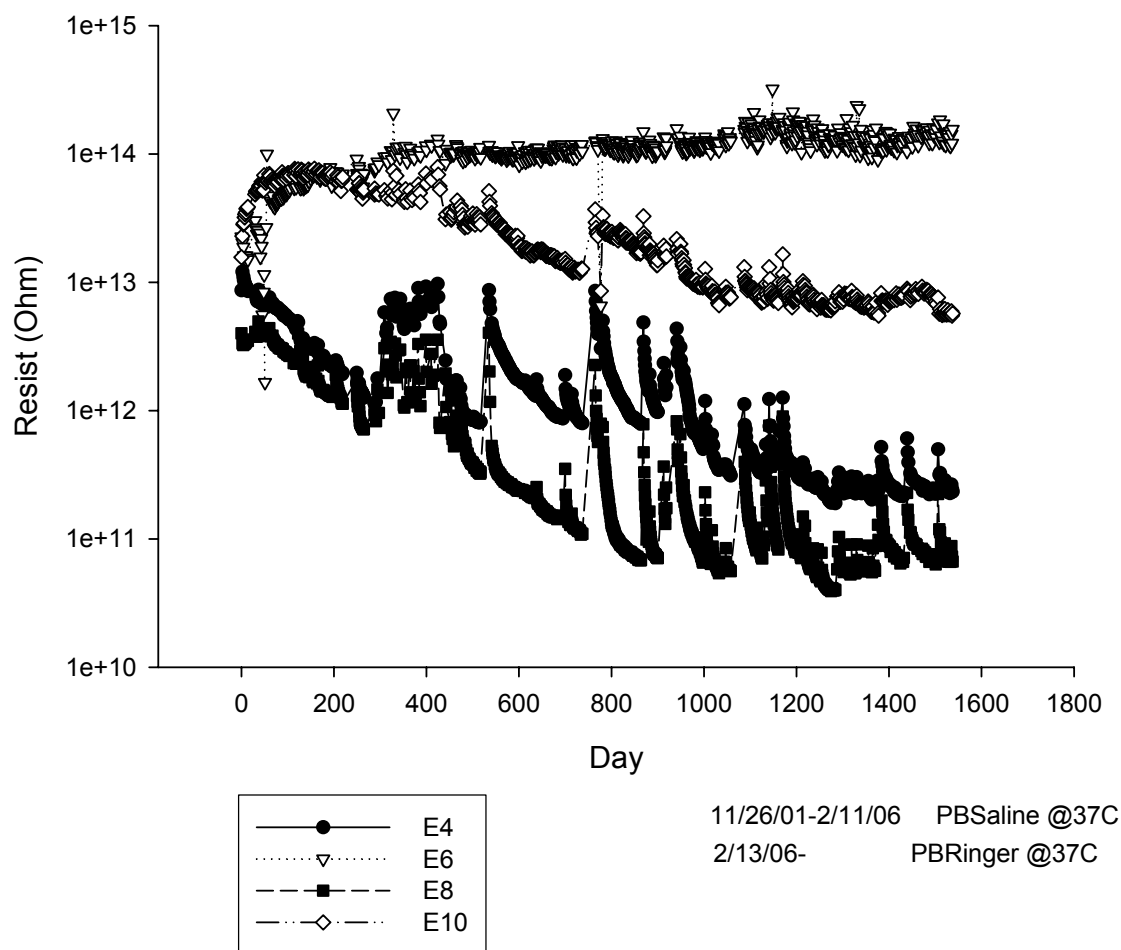


a_LCP010921Ae10_starfish_20xEPIDFback,
a_LCP010921Ae08_pinhole_40xEPIDFfront).

LCP010921B was the second set and were coated with MED4-4220. Belden 32AWG Teflon insulated wires were soldered onto the contact pads by Kester water-soluble solder, and solder flux was cleaned with DIH₂O/Isopraponal in ultrasonic cleaner at 50°C. The four devices of LCP010921B were then coated with MED4-4220 cured at 125°C for 2 hours. On 11/26/01, LCP010921B (E4, E6, E8, E10) began wet test in saline at 37°C. After four year and three months testing, the resistance of E6 remains at 10¹³/10¹⁴ Ω and the resistance of the rest devices decreased about one to two order of magnitude gradually with the time, E4 from 10¹² to 10¹¹ Ω (-5, +5V), E8 from 10¹² to 10¹⁰ Ω (-5, +5V), E10 from 10¹³ to 10¹² Ω (-5, +5V) respectively. There is no sign of corrosion in LCP010921B and pass test for this set of the devices is continuing.



LCP010921B



Third Batch - LCPIDE030603

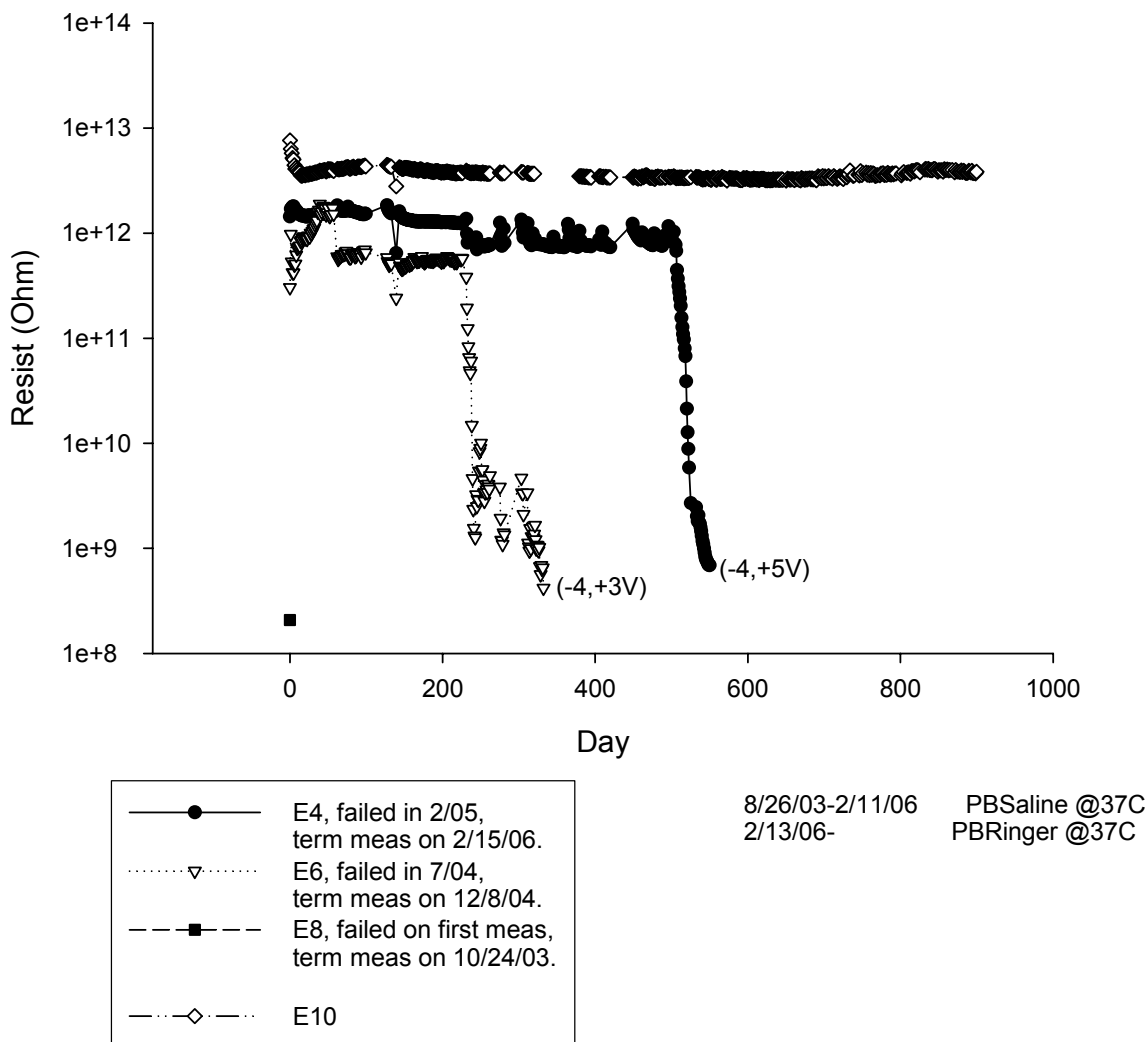
LCPIDE030603 was the third batch of LCPIDE samples from Foster-Miller with new LCP materials. Rogers R-flex® 3600 is a thinner LCP with whiter color, and Rogers R-flex® 3800 is a thicker LCP with darker color. In this experiment, four triple tracks devices (LCPIDE030603WE4, E6, E8, E10) were assembled with the thinner LCP Rogers R-flex® 3600, and other four (LCPIDE030603DE4, E6, E8, E10) were assembled with the thicker LCP Rogers R-flex® 3800. The assembly procedure was the same as LCP010921B and all the LCPIDE030603 devices were encapsulated with MED4-4220 cured at 125°C for 3 hours.



On 8/26/03, LCPIDE030603W & LCPIDE030603D began wet test in saline at 37°C. LCPIDE030603WE8 failed the test right way. Microscopic exam revealed that corrosion occurred at the exact location where the air bubble in silicone was found before the test (b_LCPIDE030603WE08_siliconeBubble_A42-B41L_20x & a_LCPIDE030603WE08_Corr_B41-A42_DF5x). It is also noticed that MED4-4220 used in this experiment behaved like quick cure silicone and thus thickened rapidly high, therefore easier to trap air bubble. The second failed device on the thinner LCP is LCPIDE030603WE6. The resistance of this device began at $10^{11} \Omega$, gradually dropped to $10^9 \Omega$ within 11 months test period, and remained at $10^8 \Omega$ with very limited bias range for another three months before completely failing. Triple tracks looked very clean after the test; however, microscopic exam revealed two spots of corrosion. One spot seemed to be early stage dendrite corrosion, which may be caused by electrolysis of Au under the bias at defect spot of silicone coating (a_LCPIDE030603WE06_diffCorr_A32-B32MR_DF20x). On the second spot, a bridge was formed between the traces and the problem seemed to come from lint contamination (a_LCPIDE030603WE06_lintCorr_B18-A19-B19MR_DF20x). The third failed device was LCPIDE030603WE4. After 18 months testing, the resistance of LCPIDE030603WE4 gradually dropped from 10^{12} to $10^8 \Omega$. The measurement for the device was terminated on 2/15/06. Microscopic exam showed a spot of dendrite corrosion (a_LCPIDE030603WE04_diffCorr_A14-B14M_DF20x & DF5x). The mark on the Au suggested the electrolysis of Au might be the cause for the corrosion. The greenish corrosion of Cu on the leads was also observed; however, neither bridge between the leads nor the leakage path can be identified. Finally, the resistance of LCPIDE030603WE10 remains at $10^{12} \Omega$ after 30 months measurement and the pass test is currently continuing for this last Rogers R-flex® 3600 device.



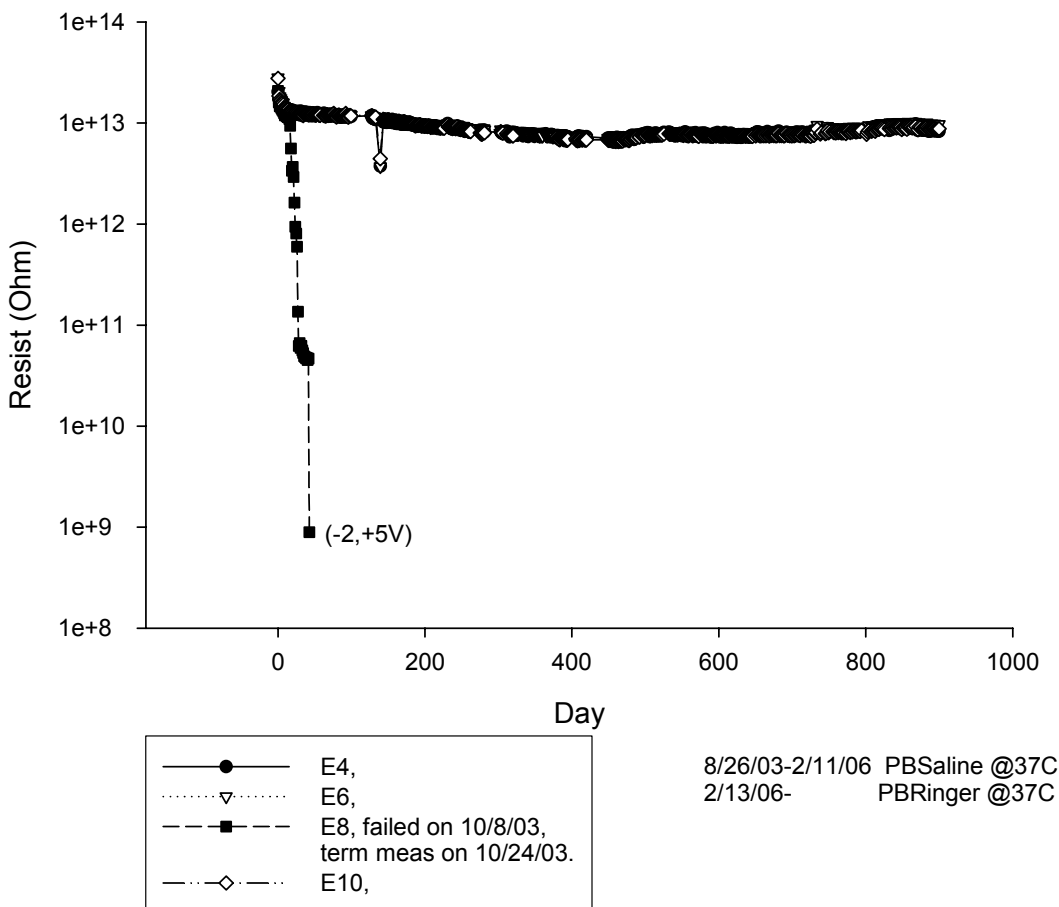
LCPIDE030603W



As for LCPIDE030603D Rogers R-flex[®] 3800 samples, the resistance for the most devices (LCPIDE030603DE4, E6, E10) has remained high from 2×10^{13} to 7×10^{12} Ω after 30 months test. The pass test for these devices is continuing. So far, the only Rogers R-flex[®] 3800 device failed is LCPIDE030603DE8. After less than one and half month testing, the resistance of LCPIDE030603DE8 quickly dropped from 10^{13} Ω (-5, +5V) to 10^8 Ω (-2, +5V). Microscopic exam showed the dendrite corrosions at location of A57-B57M (a_LCPIDE030603DE08__discolor_A57-B57M_DF20x).



LCPIDE030603D



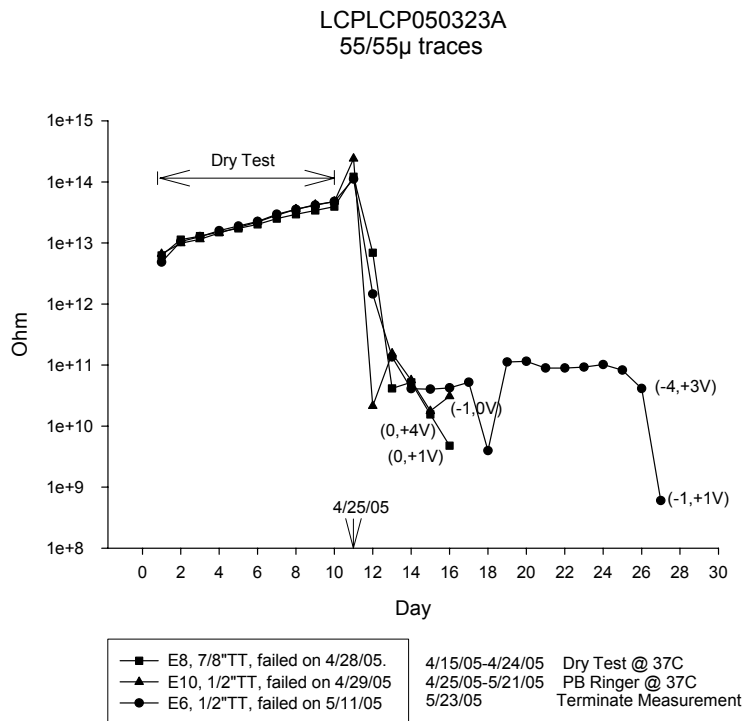
LCP IDEs with LCP and Parylene coatings

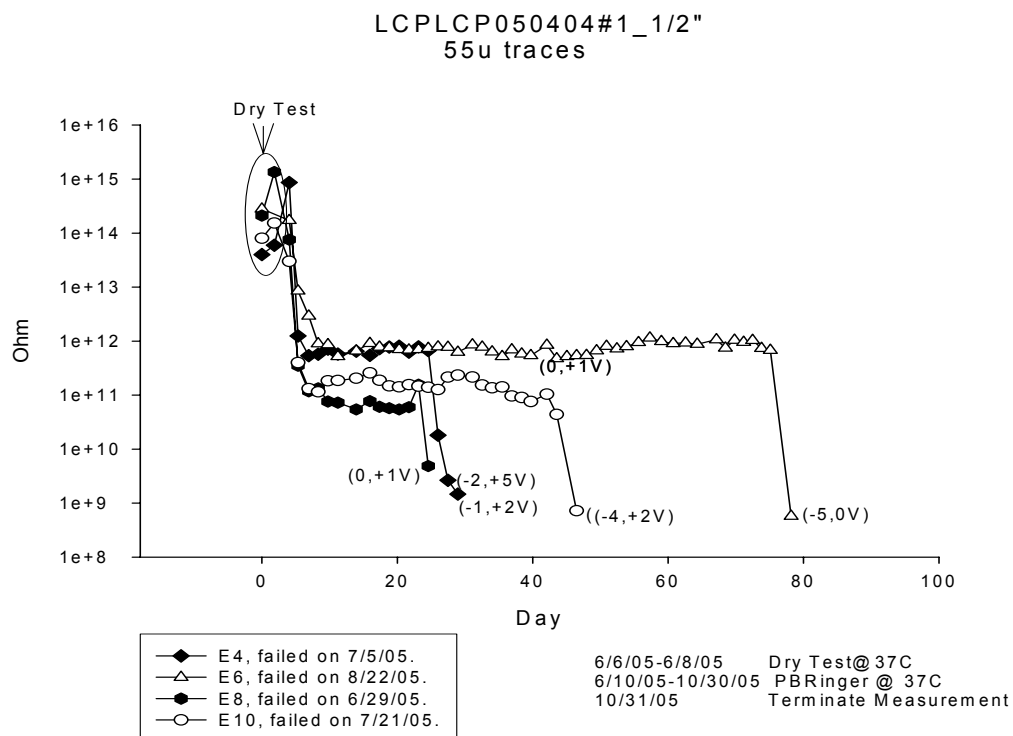
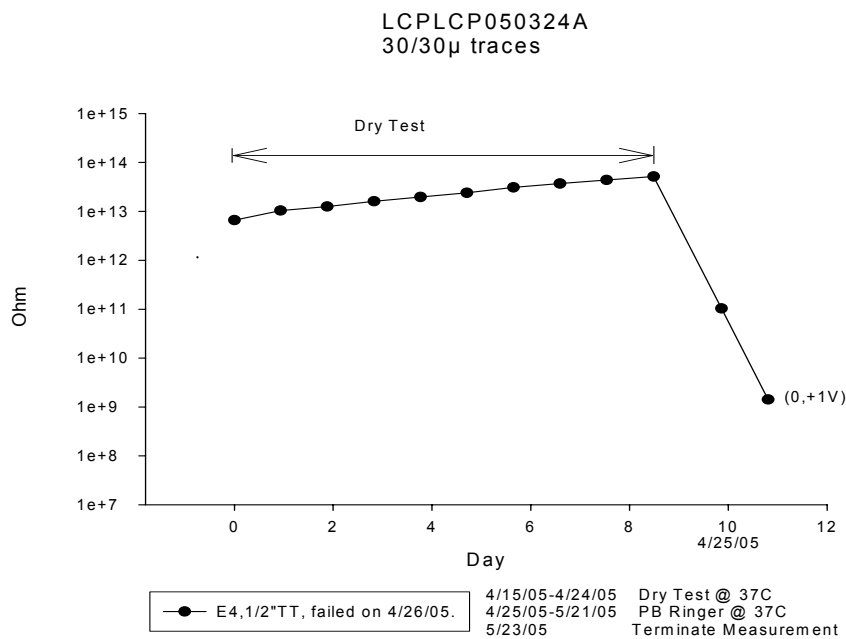
Several sets of inter digitated electrodes (IDEs) on LCP substrate insulated with either LCP or Parylene coating from Foster Miller were examined. All the samples were initially glued onto microscope slides and 30AWG Teflon insulated Belden wires were connected onto the contact pads with H20E silver epoxy cured at 120⁰C for 30 minutes. The samples were then slid through precut slot on a test jar's green cap and were fixed with MED2-4220 quick cure silicone at a position such that contacts were outside of test jars. The Belden wires were finally soldered onto DB25 pin connector for pass test measurement.



LCPLCP050323A, LCPLCP050324A, LCPLCP050404#1, #3, & #4

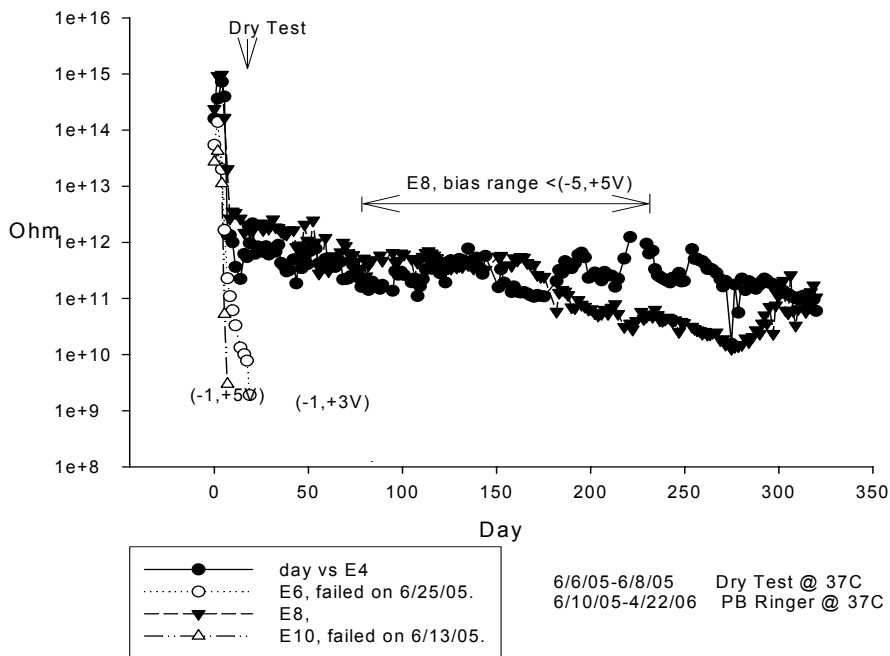
LCP-LCP samples are IDE on LCP insulated with another layer of LCP. After few days dry test, samples began wet test in PB Ringer. The experiment results show that in general the samples with 30 μ /30 μ traces fail faster than 55 μ /55 μ TT devices. Also, the samples with shorter triple tracks section (1/2" and 7/8"TT) often survive longer than the samples with longer TT (1 1/4"). Up to 4/22/06, most of LCP-LCP devices have failed and LCPLCP050404#1_7/8" is the only sample currently continuing its test. While the cause of failure is not obvious for some devices, microscopic exam does show pinhole defects and lint contamination on the others (e.g. LCPLCP050404#3 & LCPLCP050404#1_500.) The experiment results are summarized in following plots.



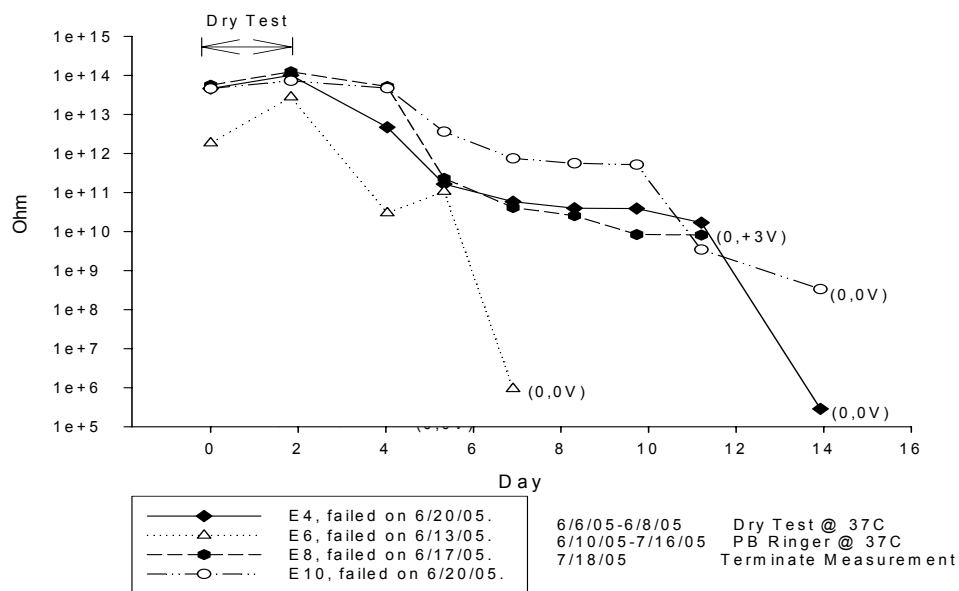




LCPLCP050404#1_7/8"
55/55u traces

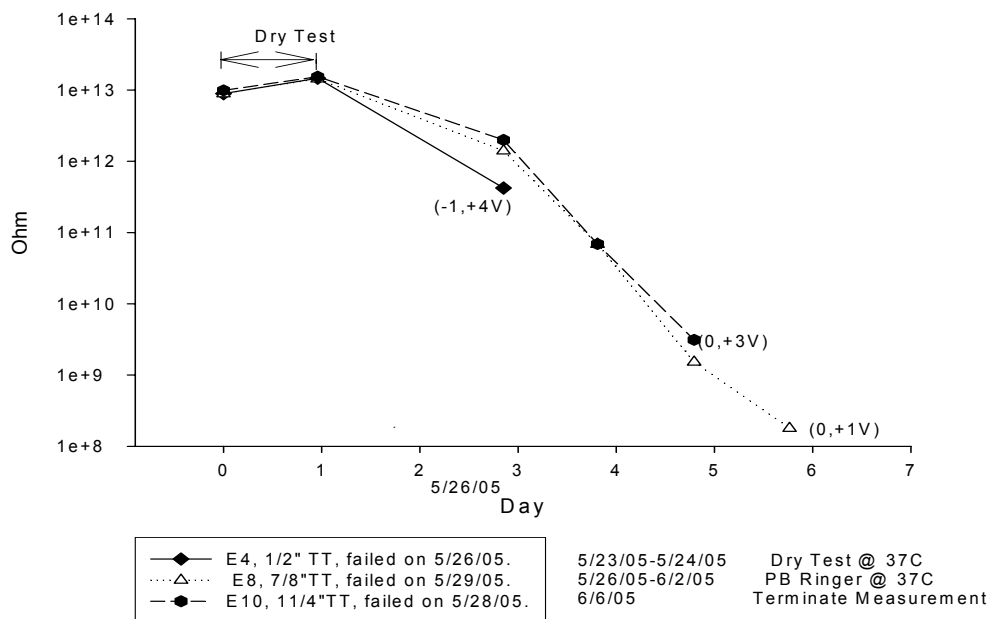


LCPLCP050404#1_11/4"
55/55u traces

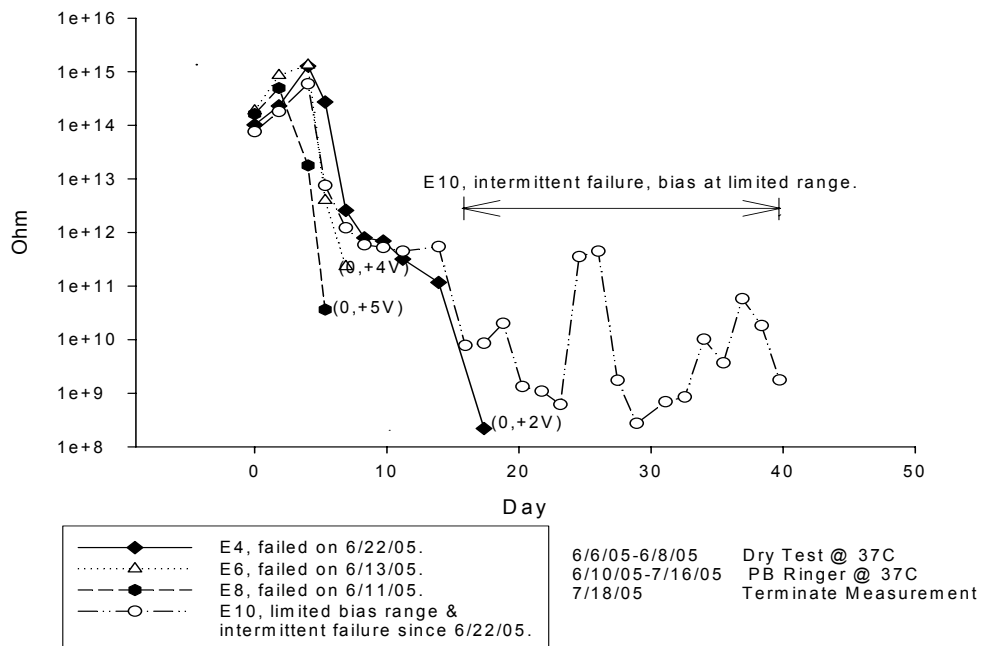


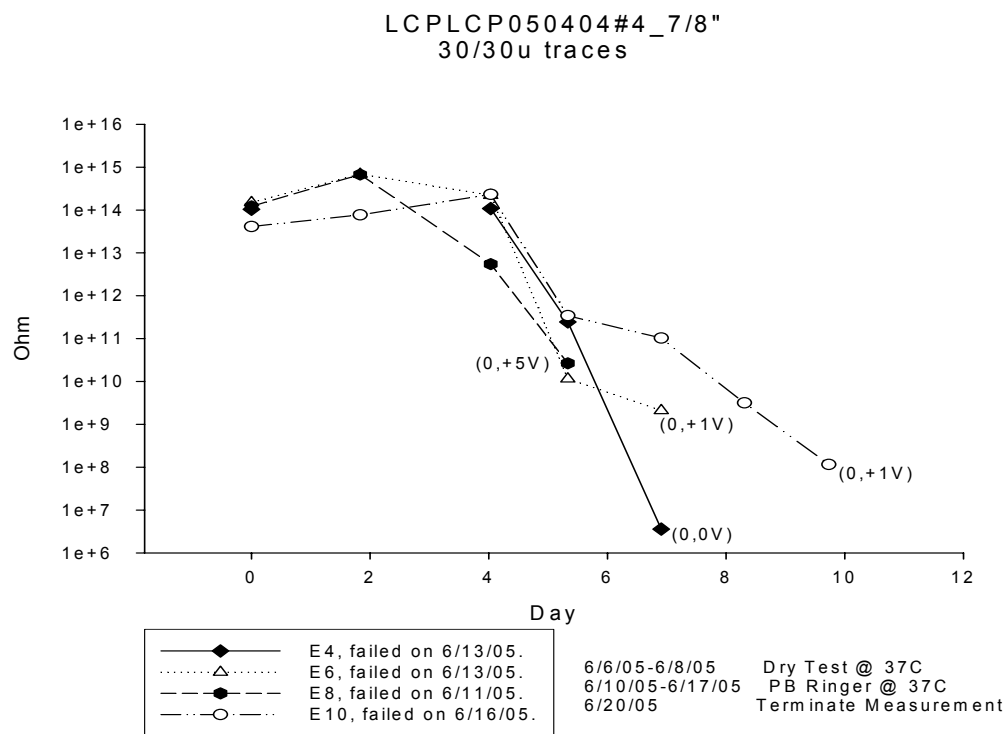


LCPLCP050404#3_1/2"_7/8"_11/4"
30/30μ traces



LCPLCP050404#4_1/2"
30/30u traces





LCPPAR050323#2, LCPPAR050324#5, #6, #7

LCPPAR050323#2 (11/4"TT) and LCPPAR050324#5(1/2"TT), #6(1/2",7/8",11/4"TT), #7 (1/2",7/8",11/4"TT)are IDE on LCP insulated with 1 μ Parylene. Devices began dry test on 5/23/05. Two-day measurements showed the resistance of 10^{12} to $10^{13}\Omega$. On 5/26/05, PB Ringer was added to the test jars. All the 1 μ Parylene insulated devices failed on the first wet measurement.

LCPPAR050404#2

LCPPAR050404#2(1/2",7/8",11/4"TT)& #5(1/2",7/8",11/4"TT) are IDE on LCP insulated with 5 μ Parylene. After 2-day dry test on 6/10/05 for #2 and 6/20/05 for #5, samples began wet test in PB Ringer. All the devices insulated with 5 μ Parylene failed or began to fail on the first wet measurement. Corrosion was observed on all TT sections.

LCPPAR5u060106

LCPPAR5u060106(7/8"TT) is IDE on LCP insulated with 5 μ Parylene by AST Products, Inc. Microscopic exam showed that some of Au/Cu traces were not covered



with Parylene. On 3/23/06, the sample was put under pass test in PBRinger at 37°C and failed on the first measurement. A further microscopic exam confirmed corrosion on uncovered Au/Cu traces.

CVD Ceramic Surface Coating Testing In-Vitro

Ring square sample RSN25A for evaluating silicone CV2500 insulation over Si substrate were assembled. The devices were put under pass test since 3/19/97. The experiment results are summarized in Table 1.

Time Period	
3/19/97-(3/9/98-4/29/00)- 11/8/00 11/30/00-12/13/02	E4 $9 \times 10^{11} \rightarrow 10^{10} \rightarrow 10^{11}$ <(-4,+5V) $10^9/10^{10}$ (-5,+5V)
12/14/02- 5/8/03 1/7/04	OverRange Quick cure MED2-4220 applied to seal TERMINATE meas. Two big Plane (1,1,1) corr on Si. Cracking of silicone jacket over yellow wire. Ag epoxy contact is found wet.
3/19/97-(7/27/97-11/8/00) 11/30/00-4/27/03 5/8/03	E6 $10^{12} \rightarrow 10^{10}$ biased at limited range $10^8/10^9$ very limited range $\rightarrow 10^9/10^{10}$ (-5,+5V) $\rightarrow 10^8$ (-3,+3V) TERMINATE meas. Small plane (1,1,1) corr scattered on Si.
3/20/97-(7/25/97-1/1/99) 2/12/99- 5/8/03	E8 $10^{12} \rightarrow 10^{10}$ biased at limited range OverRange TERMINATE meas. Severe plane (1,1,1) corr along inside edge of the ring and crack between silicone layers are observed.
3/20/97-(7/25/97-6/7/00) 6/9/00-10/27/01 (12/8/01-12/18/02)-4/27/03 5/8/03 5/13/03-2/11/06 2/14/06	E10 $1.5 \times 10^{12} \rightarrow 10^{10}/10^{12}$ mostly (-5,+5V) 10^9 (0,+5V) \rightarrow (-4,+5V) \rightarrow (0,+5V) $10^9/10^{10}$ (-5,+5V) $\rightarrow 10^8$ (0,+5V) crack btw silicone layers are observed, quick cure MED2-4220 applied to seal OverRange TERMINATE meas. Cracks in silicone insulation outside ring.

Table1. RSN25A Measurement Summary



On 5/8/03, devices E6 and E8 were terminated from the pass test. After E6 & E8 are extracted from the test tube, pictures were taken with “as is” as well as with CV2500 removed from the testing area. While severe plane (1,1,1) corrosions were observed along the ring of E8, it was found that pitting corrosions spread throughout the testing area of E6. As indicated in Table1, devices E6 & E8 could begin to fail as earlier as 7/97. Poor adhesion between CV2500 and Si, which might be caused by insufficient cleaning of Si substrate prior to assembly, apparently was the cause to E6’s failure. The stress of CSV2500 along the ring, on the other hand, was believed the reason for E8’s corrosion. Moreover, local delamination between top and bottom silicone layers in the sandwich structure of RSN25A (silicone/Si /silicone) was found in E8 and apparently was another reason for the sudden failure of the device after nearly two years measurement.

On 5/8/03, no apparent corrosion was found on Si for E4&E10, although the electrical measurements indicated both devices also failed. A further exam found that the sandwich structure of E10 cracked between top and bottom silicone layers. Quick cure silicone MED2-4220 were applied on the sides of both devices E4 & E10 to seal any existing and possible cracks and pass test measurements were continued.

Since the repair, both E4 & E10 continued measured at over range. On 1/7/04, E4 was terminated from the pass test and several big plane (1,1,1) corrosion spots were found on Si surface. It was possible that local defects already existed at interface of CSV2500/Si and the repair process on 5/8/03 may magnify the trouble at these areas. Moreover, wet Ag epoxy contact and a greenish corrosion spot on the yellow wire caused by cracking in silicone jacket over the wire were also observed. This defect spot over the wire may had already occurred before the repair and was apparently responsible for the failure of E4 after 5 year and 9 months measurement as well.

After E10 was terminated from the pass test on 2/6/06, the device was thoroughly examined under microscope. Although no corrosion was found on Si of the testing area, cracks in silicone outside ring as well as an air bubble in silicone coating over the wire provided leakage path. Corrosion at contact region and on Si at cracks was observed. Multiple failures in silicone encapsulation explained the reason for E10’s



failure after nearly three year and three month measurement and also explained the reason of continued failure of the device after repair.

In conclusion, while poor adhesion of CV2500 over Si surface was one of the problem in this experiment, another reason for the failure of RSN25A devices was apparently caused by failed silicone encapsulation outside ring area. Cracks, trapped air bubbles, and delaminated silicone layers in the sandwich structure provided undesirable leakage paths other than failed CV2500 coating itself.

Silicon wafers coated with SiC or SiC+Parylene.

One set of four, SiC and SiC+Parylene samples were assembled prior to testing. The assembling procedures are described briefly as follows. A ¼" I.D. O-ring used as defining test area was first glued onto test surface with silicone MED4-4220. A silicone insulated wire (28AWG, Bay Associates) used as lead to external testing equipment was then connected onto backside of the wafer with Ag epoxy H20E. The partial assembled sample was finally placed in a Teflon mold with O-ring facing down, filled with silicone MED4-4220, and cured at 150°C for 3 hours.

Microscopic inspection showed that the surface of the silicon carbide samples had many particle like defects. The surface morphology for SiC with Parylene was much smoother, however few discolored spots are found on SiC+Parylene samples. Pictures for both types of the samples were taken before test at magnifications of 5x or 40x.

The samples were put under test at 37°C on 2/8/06. The three-day dry test verified system function at the $10^{14}/10^{15} \Omega$ range for a sweep voltage of -5 to +5V. After the test tubes were filled with phosphate buffered Ringer solution on 2/13/06, all SiC samples failed at the first measurement cycle, $10^9 \Omega$ (-5,+2V). RSUTAH051207SiC was terminated from the pass test on 3/2/06. A further microscopic exam showed "blisters" on SiC film. On the other hand, all SiC+Parylene samples have maintained the resistance of $10^{14} \Omega$ with full sweep of (-5, +5V) after 9 weeks wet measurement. Measurements are currently continuing for the SiC-Parylene samples.



It is likely that the small defects in the SiC films allowed saline infiltration and subsequent micro-corrosion. The “blisters” may have been caused by corrosion of the silicon underlying the SiC initiated by the small defects.

Silicon Nitride Coatings on Silicon Substrates

LPCVD or PECVD deposited dielectric film combinations of silicon nitride and silicon dioxide on thermally oxidized Si or bare Si substrates were assembled into eight sets of ring square samples. The samples were put under test at 90°C on 8/22/05. After initial 12 days dry measurement to verify the system functioning properly, the test tubes were filled with phosphate buffered Ringer solution to begin wet measurement on 9/9/05. The pass test results up to 4/22/06 are summarized in Table 1 and explained as follows.

RS050524N1 (Si+1391.8Å thermal SiO₂+2148.80Å LPCVD SiN)

The pass test measurement showed three of the RS050524N1 devices (E6, E8, E10) had an asymmetrical IV since the beginning of the wet measurement, which indicated electrochemical corrosion process undertaking due to exposure of Si substrate at defects in passivation layers. Si oxidizes when bias negatively and reduces at positive sweep, therefore devices show more hermetic at the negative range (typically 10¹²Ω) and high leaky at positive bias (typically 10⁹Ω). Plane (1, 1, 1) corrosion was indeed found on these devices and pass test measurements were terminated on 11/2/05. Although Plane (1, 1, 1) corrosion is also observed on the device E4, E4 did not show asymmetrical IV. Instead, the resistance of E4 maintained at 10¹²Ω for almost three month wet measurement and then suddenly dropped to 10¹⁰Ω and 10⁸Ω subsequently. Pass test measurement of E4 was terminated on 1/23/06. Color change was observed on all RS050524N1 devices, indicating natural erosion of SiN film in ringer solution.

RS050524N2 (Si+1372.6Å thermal SiO₂+2169.80Å LPCVD SiN+1μmLTO)

While RS050524N2 (E4, E6) devices have maintained resistance at 10¹¹/10¹²Ω with full sweep of (-5, +5V) after four months measurement in PB Ringer, the resistance of RS050524N2 (E8, E10) suddenly dropped from 10¹²Ω to 10⁸Ω after two months measurement. Microscopic study showed all RS050524N2 devices had spots of defect



in their films yet there is no apparent difference between failed devices (E8 & E10) and good devices (E4 & E6). A further examine in the capacitance measurement showed that both E8 and E10 had phase shift from 89.6° to 79° , indicating resistive characteristic, therefore more leakage, occurred in the dielectric films. There is no obvious color change for RS050524N2 devices. As expected, SiO_2 layer has stabilized SiN film. Pass test measurement for RS050524N2 (E8, E10) has been terminated on 1/23/06 and is continuing on E4 and E6 currently.

RS050524N5502-15 (Si+1279.60Å thermal SiO_2 +2133.8Å LPCVD SiN+1µmLTO),
Same as RS050524N2

Most of RS050524N5502-15 devices (E4, E6, E8) have maintained resistance at $10^{11}/10^{12}\Omega$ with full sweep of (-5, +5V) after almost eight and half months measurement in PB Ringer. However, the resistance of RS050524N5502-15 (E10) suddenly dropped from $10^{12}\Omega$ to $10^8\Omega$ and failed pass test after three months measurement. Similar to RS050524N2, there is no color change in the dielectric films and spots of defect were observed on all films with no exceptional difference in devices E10. Capacitance measurement of E10 indicated phase slightly shifted from 84.4° to 80.6° after 4 month test. Pass test measurement for E10 has been terminated on 1/23/06 and is continuing on E4, E6, and E8 currently.

RS050524N3 (Si+1613.34Å thermal SiO_2 +5000Å PECVD SiN)

All RS050524N3 devices showed discoloration spots caused by defects in SiN films due to surface contamination such as flake and particles during film deposition process. While device E6 showed asymmetrical IV at the beginning of the wet measurement, devices E8 and E4 maintained at $10^{11}/10^{12}\Omega$ for a period of 1.5 months and 3.5 months respectively before they also showed asymmetrical IV. Asymmetrical IV indicated electrochemical corrosion process undertaking due to exposure of Si substrate at defects in SiN film. Microscopic exam confirmed the corrosion on all three devices and the degrees of the corrosion were consistent with the IV measurements. While E6 showed a cluster of plane (1,1,1) corrosion, E8 had one site of plane (1,1,1) corrosion and one spot of discoloration. The defect found in E4 after two months wet measurement remained same for the rest of 5 months testing period. Device E10 failed



in a more straight way. After measured at high $10^{11}\Omega$ for a period of 21 days, the resistance of E10 suddenly dropped to $10^9\Omega$. Several discolored sites, some caused by flake contamination and the others by pinhole defects during film deposition process, were observed in E10. The progression of SiN decay was evidenced by the significant color change from original light golden to green/blue in all RS050524N3 devices as well as at the flake-caused defect sites in E10 where SiN film was apparently thinner and the color changed from original light golden to bright yellow after 8 weeks measurement and subsequently to dark pink after 4.5 months test.

RS050524N4 (Si+1550 Å thermal SiO₂+ 3200Å LPCVDSiO₂+ 1534.8ÅLPCVDSiN +3001.8Å LPCVD SiO₂)

Except E8, 8.5 months measurement in ringer solution shows the rest of RS050524N4 devices having resistance at $10^{12}\Omega$ with full sweep of (-5, +5V). Device E8 had an asymmetrical IV since the beginning of the wet test and plane (1, 1, 1) corrosion was observed. Measurement for E8 was terminated on 11/2/05 and is continuing for E4, E6, and E10. Visual observation shows there is no color change in SiN films for all RS050524N4 devices. As expected, SiO₂ layer has stabilized SiN film.

RS050524N5 (Si+4515.2Å thermal SiO₂/LPCVDSiO₂+1467.6ÅLPCVDSiN+2821.6Å LPCVD SiO₂, thermal SiO₂≈1500-1600 Å), Same as RS050524N4

Similar to RS050524N4, four months measurement in ringer solution shows the three out of four RS050524N5 devices (E4, E6, E8) having resistance at $10^{12}\Omega$ with full sweep of (-5, +5V). Device E10 had an asymmetrical IV since the beginning of the wet test and small plane (1, 1, 1) corrosion sites were observed on this device. Pass test measurement for E10 was terminated on 11/2/05 and is continuing for the rest. Again there is no color change in SiN films for all RS050524N5 devices.

RS050524N6 (Si+1611.9Å thermal SiO₂+5000Å PECVD SiN+1µmLTO)

After devices E4, E6, & E8 of RS050524N6 were measured at $10^{12}/10^{11}\Omega$ (-5, +5V) for one, four and three weeks respectively, resistances of these devices suddenly dropped to $10^9/10^8\Omega$ with limited bias range. Cracks between discolored spots were found on E4 and discolored spots only were observed on E6 and E8. Discoloration apparently was



caused by corrosion process at pinhole defects in dielectric films. The pass test measurements for E4, 6, & 8 were terminated on 11/2/05. Device E10 maintained at $10^{11}/10^{12}\Omega$ for a period of two months before it showed asymmetrical IV and plane (1,1,1) corrosion was observed in the film. E10 was eliminated from the measurement on 1/23/06. As expected, there is no color change in SiN films in general.

RS050524N8 (Si+1923.6Å LPCVD SiN+6927.20Å LPCVD SiO₂)

Devices E6 & E10 had an asymmetrical IV since the beginning of the wet test, apparently caused by pinhole defects in the dielectric films. Plane (1, 1, 1) corrosion was found on both devices and pass test measurements for E6 & E10 were terminated on 11/2/05. As for device E8, after measured at $10^{12}\Omega$ for a period of three months, the resistance of E8 dropped to $10^9/10^8\Omega$ with limited bias range. A small discolored site with cracking within was found in the dielectric film of E8 and the pass test measurement for the device was eliminated on 1/23/06. After eight months measured at $10^{12}\Omega$ with full sweep of (-5, +5V), device E4 showed asymmetrical IV. One site of plane(1,1,1) corrosion was also found in E4 and the device was terminated from the pass test on 4/22/06. Visual observation shows no color change in SiN films for all RS050524N8 devices.

HFCVD Silicone on Si Substrates

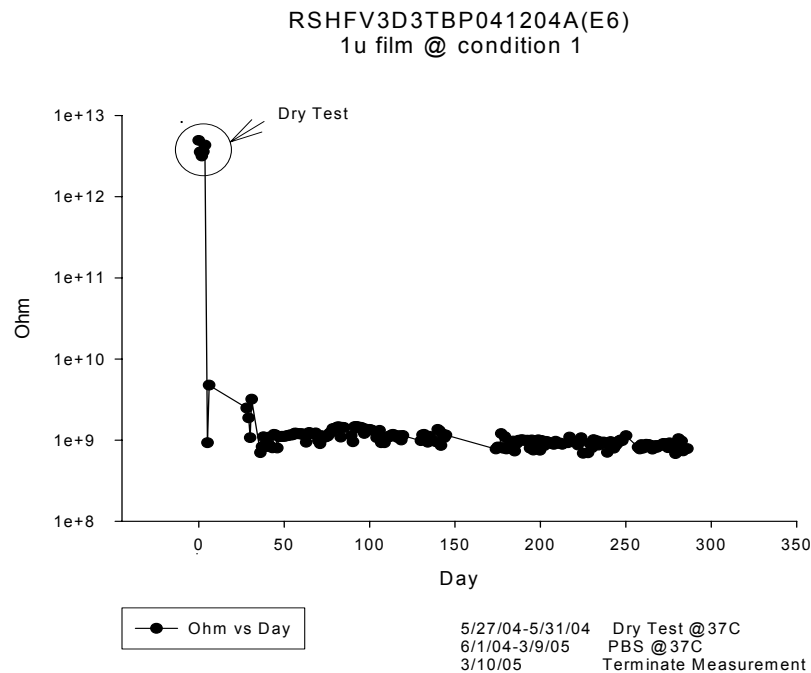
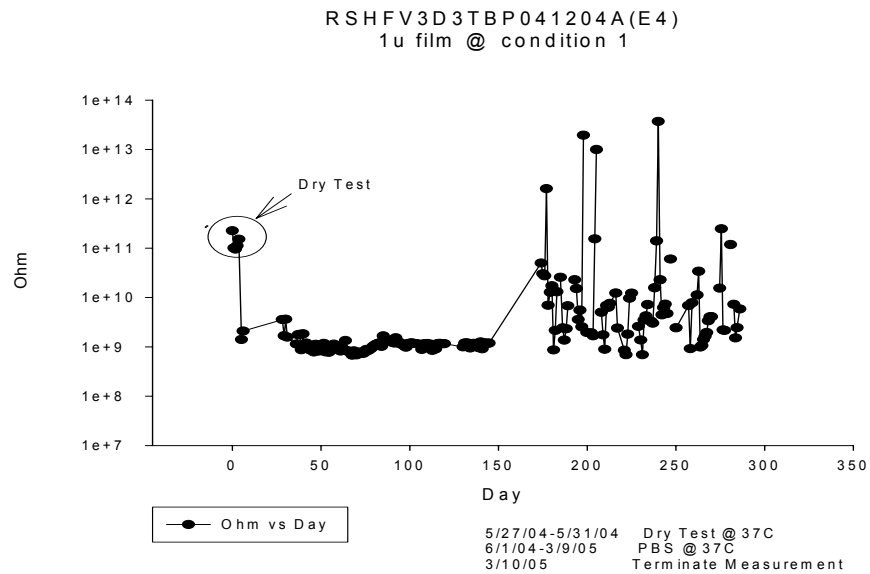
Four sets of hot filament deposited silicone film on Si substrates from V_3D_3 +TBP at two different conditions were initially examined under microscope. After assembly, the samples were put under dry test for few days to verify the system working properly. The samples were then added saline solution to begin wet test at 37⁰C on 6/1/04. Pictures of surface morphologies are taken and saved at \aa cleanroom\LabPics\RingSquare\RSHFV3D3TBP. The pass test results up to 1/7/06 are summarized as follows.

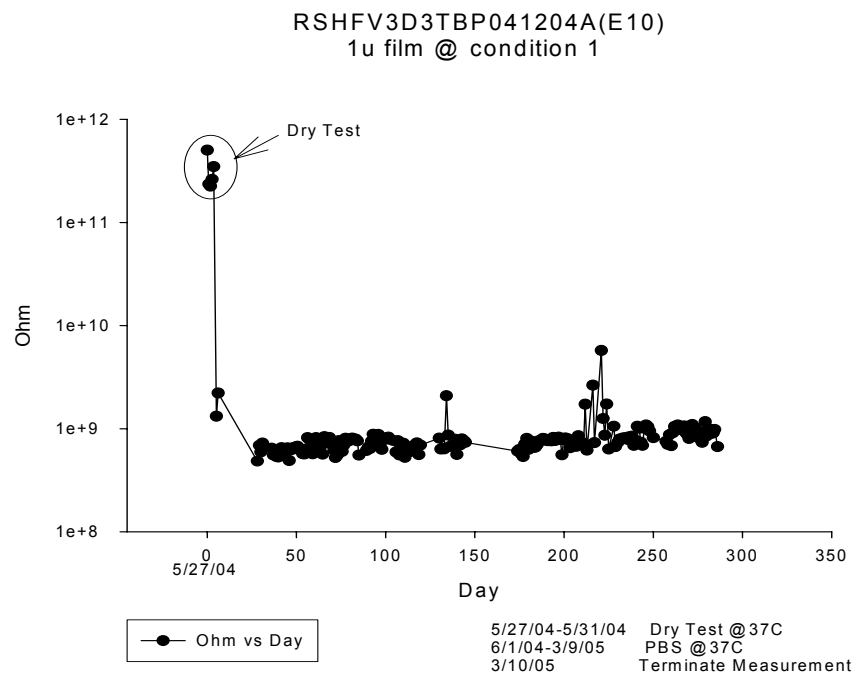
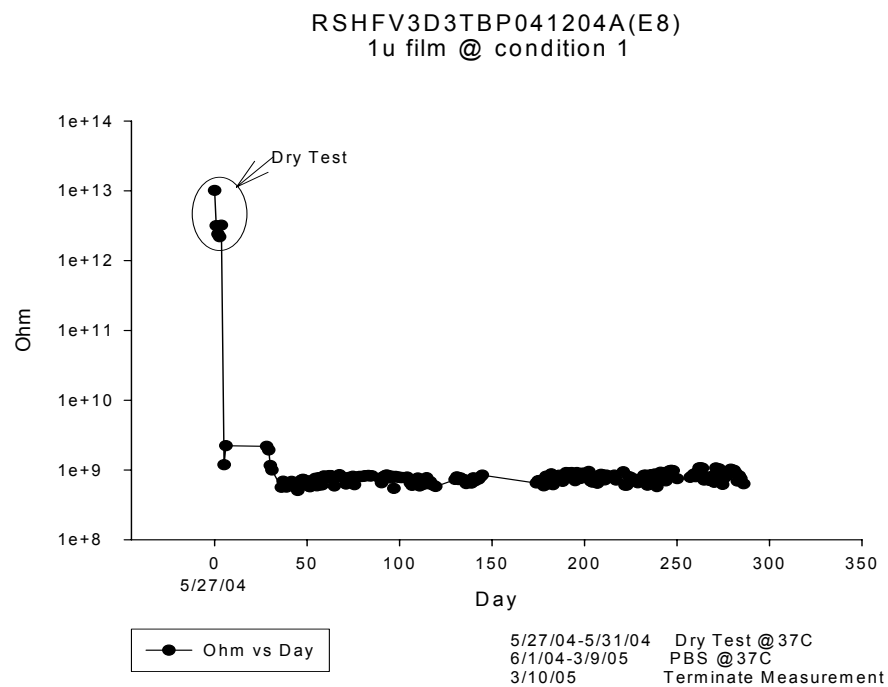
RSHFV3D3TBP041204A(E4, E6, E8, E10)

1μ film deposited at condition#1($P=300mT$, $T_f=500^0C$, $T_s=60^0C$) has the surface morphology of “star field”. The resistance data shows that in general RSHFV3D3TBP041204A has poor hermetic property. After soaking, resistance of all



four devices quickly dropped from $10^9\Omega$ to $10^8\Omega$ and the measurements were swept at limited range. The pass test was terminated on 3/10/05. Microscopic study after pass test showed extensive corrosion throughout the test surfaces, indicating general failure of the coating.



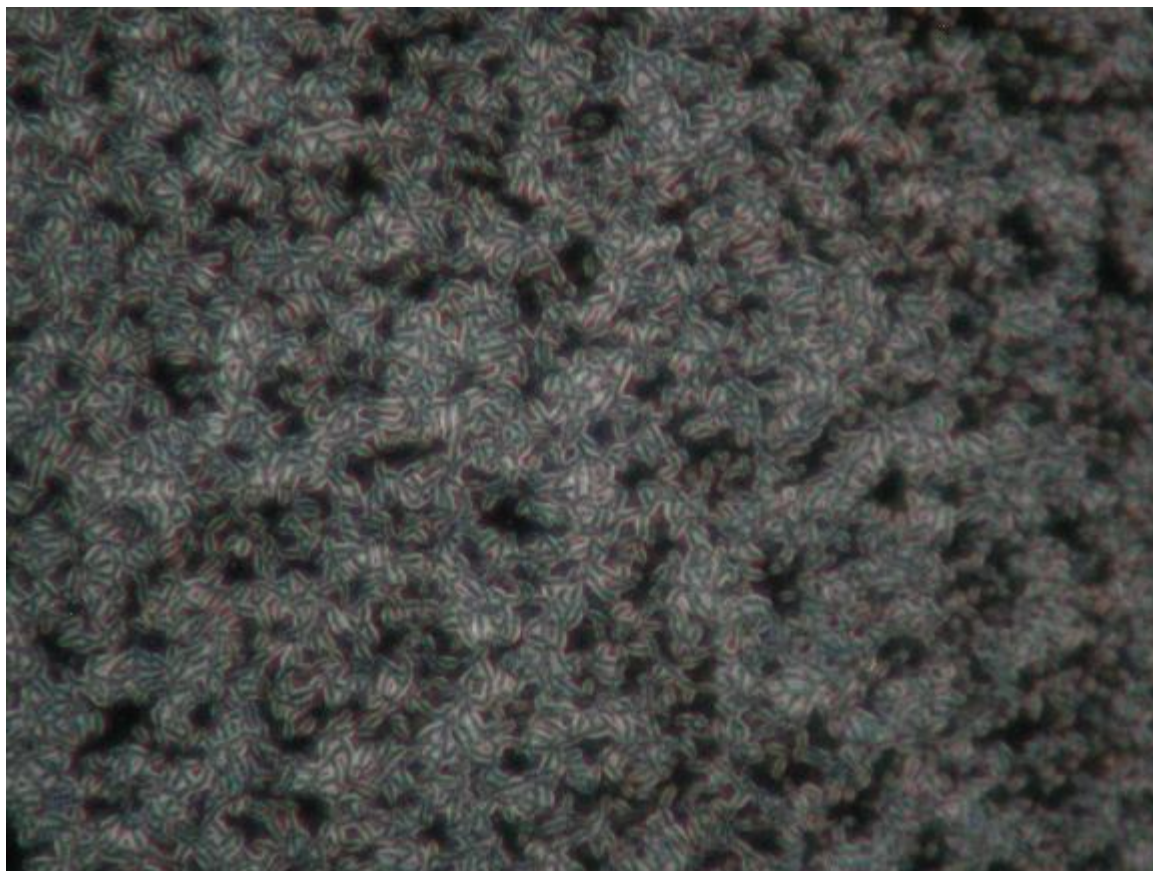




RSHFV3D3TBP041204B1(E4, E6, E8, E10) & RSHFV3D3TBP041204B2(E4, E6, E8, E10)

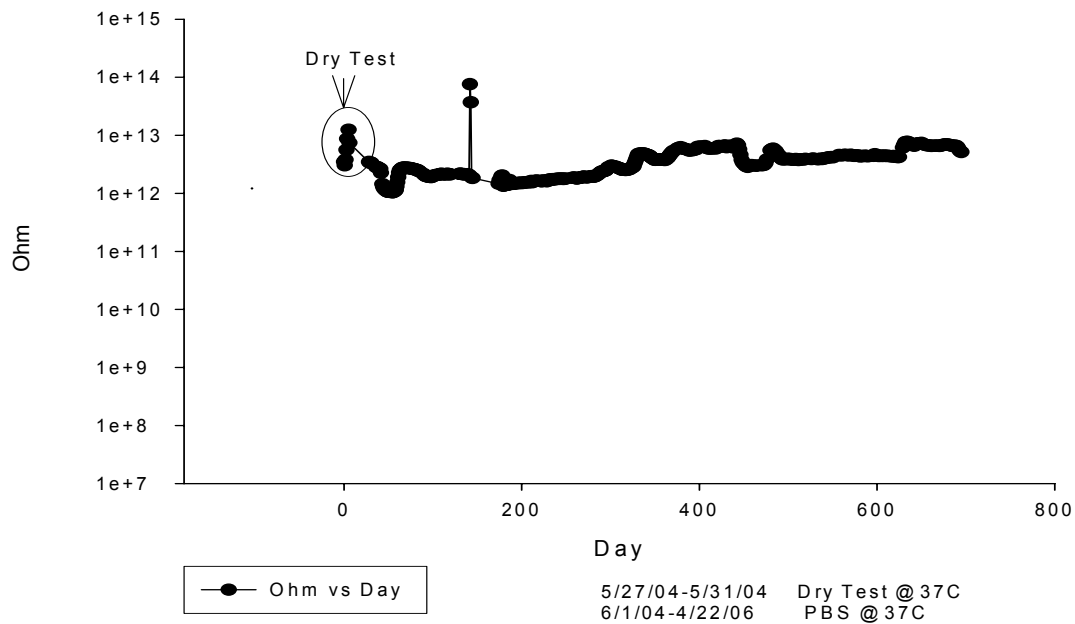
5 μ film deposited at condition#1 ($P=300\text{mT}$, $T_f=500^\circ\text{C}$, $T_s=60^\circ\text{C}$) has the “wrinkled” surface morphology. As indicated in Sigma plots, after almost 23 months soaking, five out of eight samples, RSHFV3D3TBP041204B1(E4,8,10)&B2(E6,10), keep the resistance at $10^{12}\Omega$. The other three, RSHFV3D3TBP041204B1(E6)&B2(E4,8), showed an asymmetrical IV since the beginning of the wet measurement, which indicated electrochemical corrosion process undertaking due to exposure of Si substrate at defects in passivation layer. Si oxidizes when bias negatively and reduces at positive sweep, therefore devices show more hermetic at the negative range (typically $10^{11}/10^{12}\Omega$) and high leaky at positive bias (typically $10^9\Omega$). Microscopic exams taking before and after test verified most plane(1,1,1) corrosion sites caused by defects in the deposited silicone films of RSHFV3D3TBP041204B1(E6) & B2(E4,8).

RSHFV3D3TBP041204B2 (E4) was terminated on 8/12/05 and RSHFV3D3TBP041204B1(E6) & B2(E8) were terminated on 4/22/06. The pass tests for rest 5 μ samples are continuing.



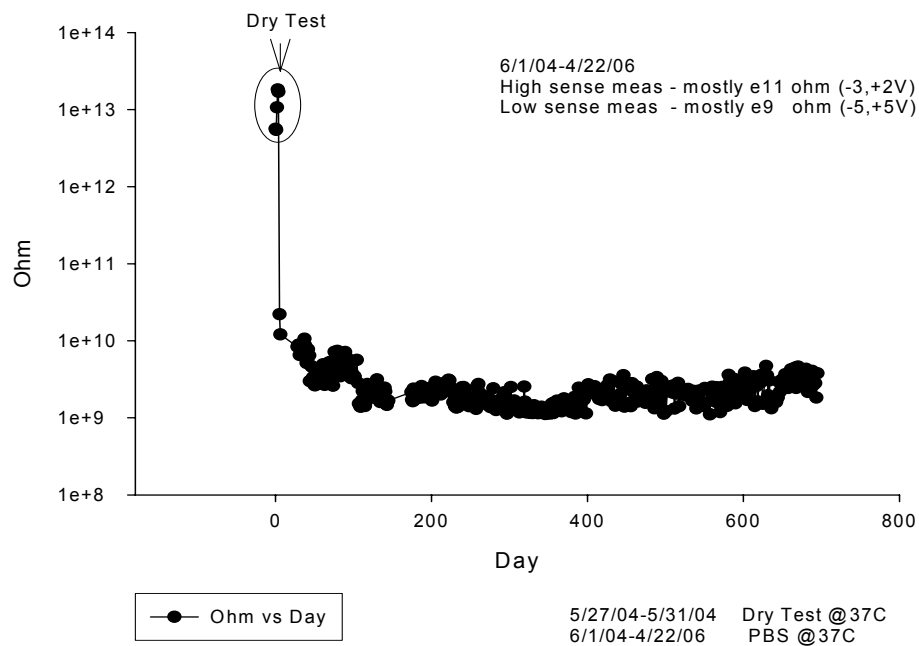


RSHFV3D3TBP041204B1(E4)
5u film @ condition 1

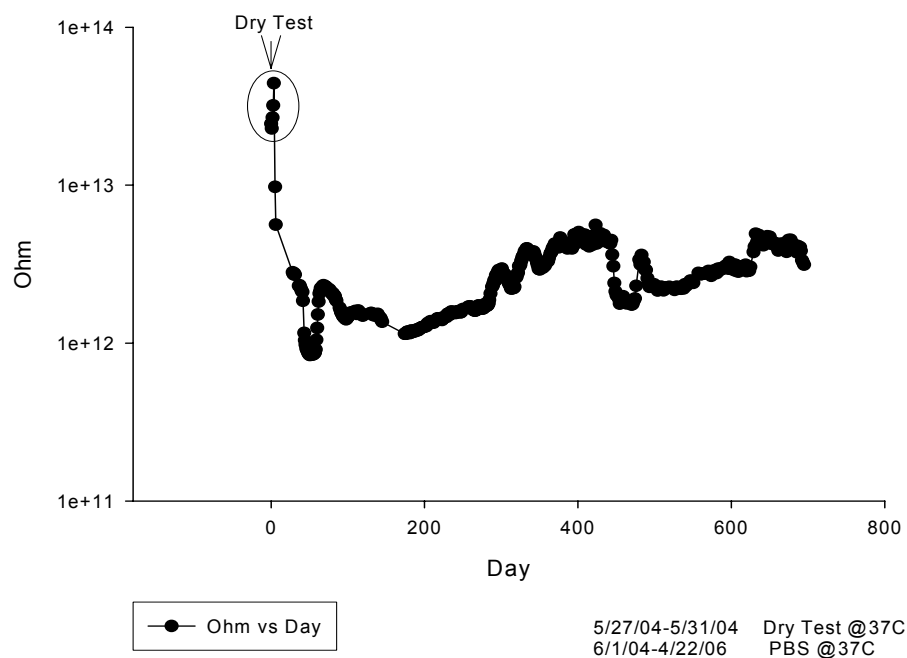




RSHFV3D3TBP041204B1(E6)
5u film @ condition 1

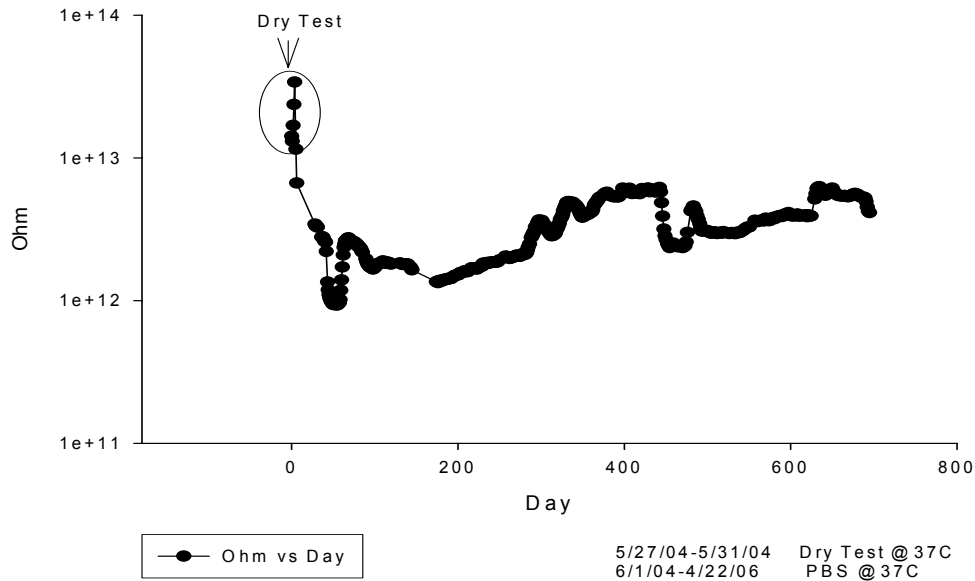


RSHFV3D3TBP041204B1(E8)
5u film @ condition 1

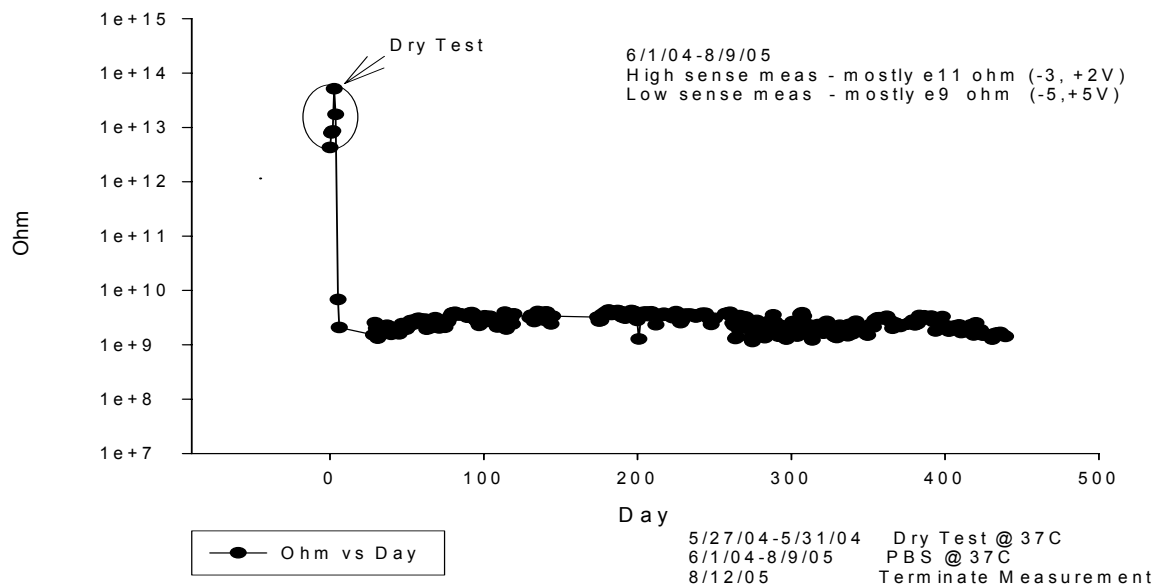


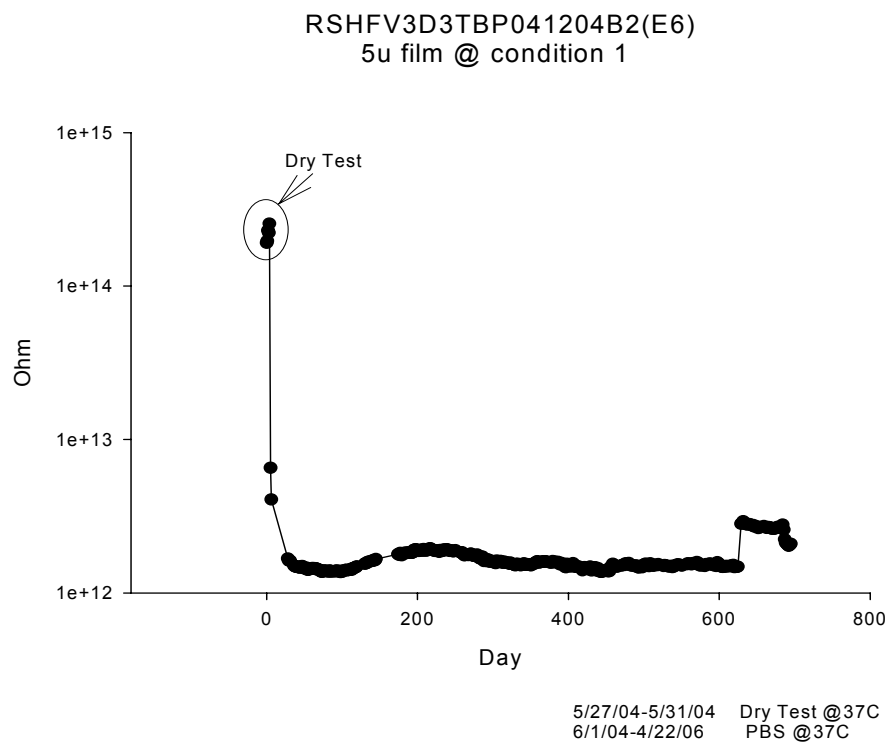


RSHFV3D3TBP041204B1(E10)
5u film @ condition 1



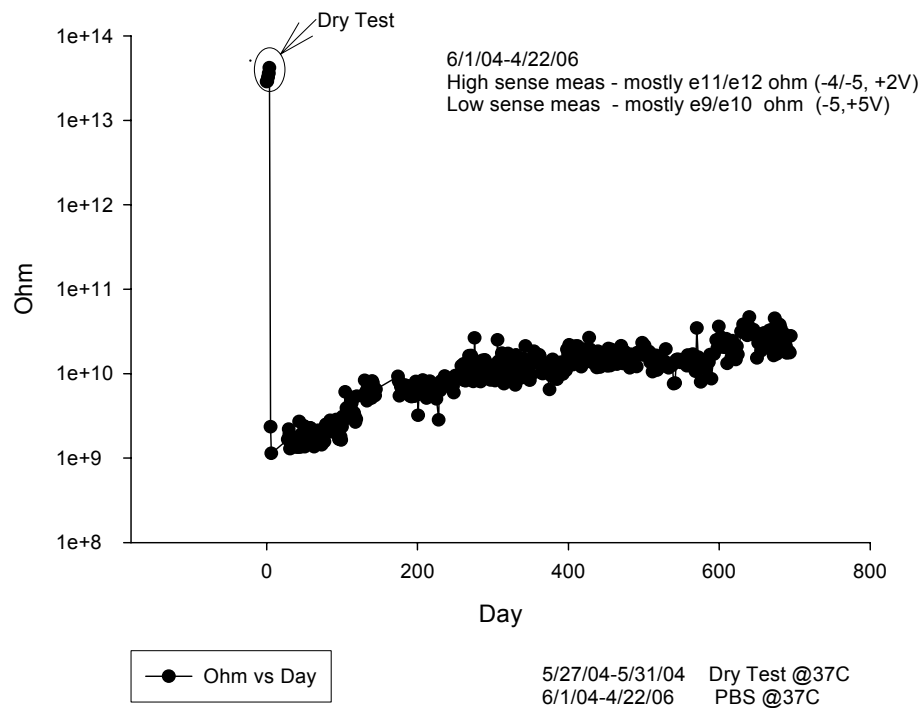
RSHFV3D3TBP041204B2(E4)
5u film @ condition 1



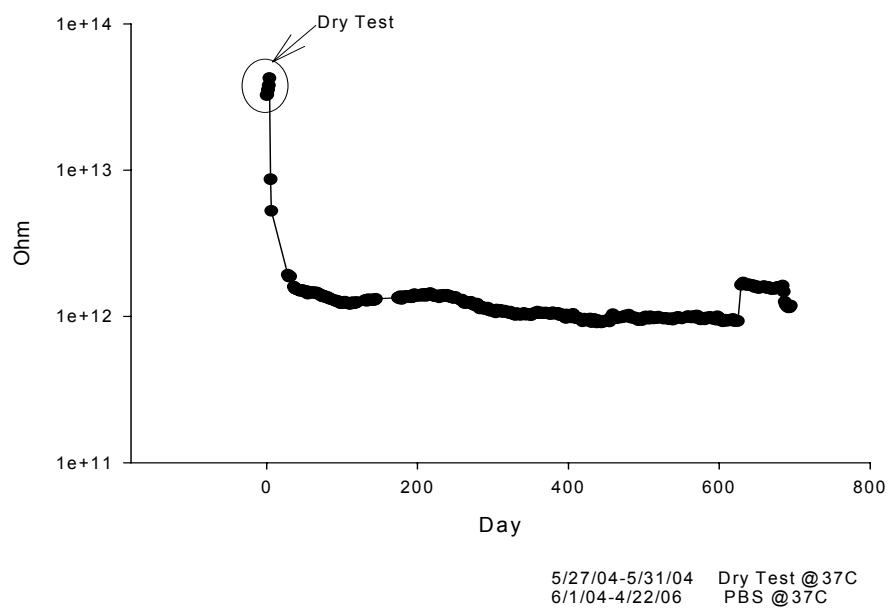




RSHFV3D3TBP041204B2(E8)
5u film @ condition 1



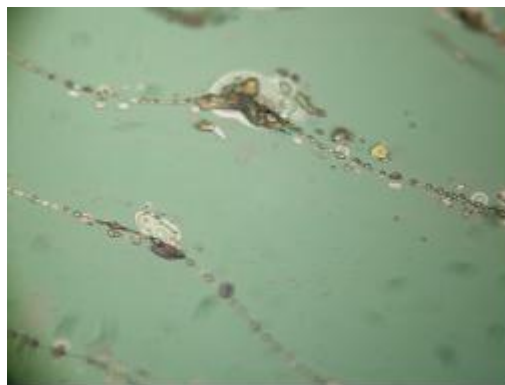
RSHFV3D3TBP041204B2(E10)
5u film @ condition 1





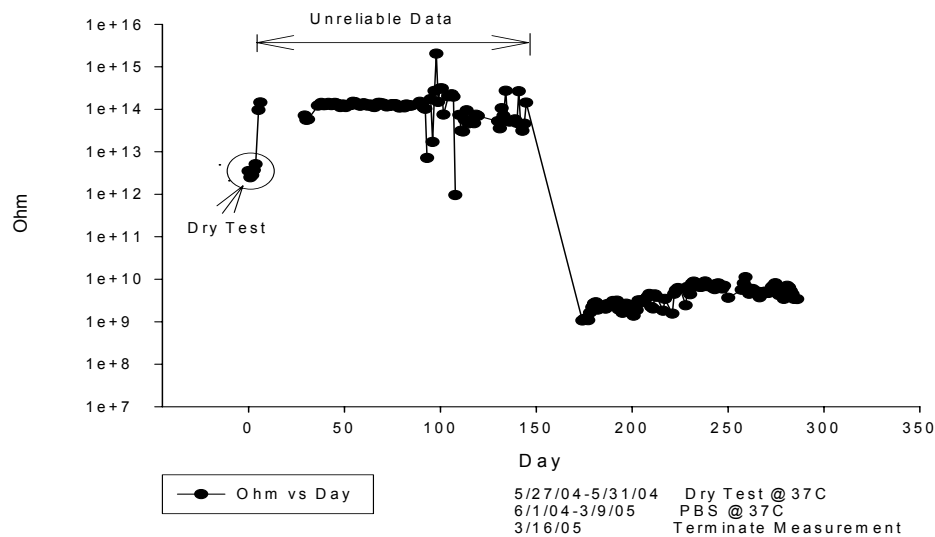
RSHFV3D3TBP041404(E4, E6, E8, E10)

1 μ film deposited at condition#2 ($P=300\text{mT}$, $T_f=400^\circ\text{C}$, $T_s=60^\circ\text{C}$) has a very smooth surface. Due to the trouble in test system, the data for the first three and half month (6/1/04-10/19/04) were unreliable. Since 11/17/04, the resistances of all four devices have continued mostly at $10^9\Omega$. While the measurements for E4 & E6 keep at full sweep (-5, +5V), the range for devices E8 & E10 has deteriorated to (-5, +3V). The pass test was terminated on 3/16/05. Microscopic analysis after pass test revealed interesting corrosion pattern that is either like a contour map or similar to pattern of clouds. A further magnified picture showed the contours are made of series of small-bead-like corrosion sites. Based on the before and after corrosion picture, it is likely that the devices were failed during the uncertain data period. The pictures were taken and saved in the file of RSHFV3D3TBP041404.

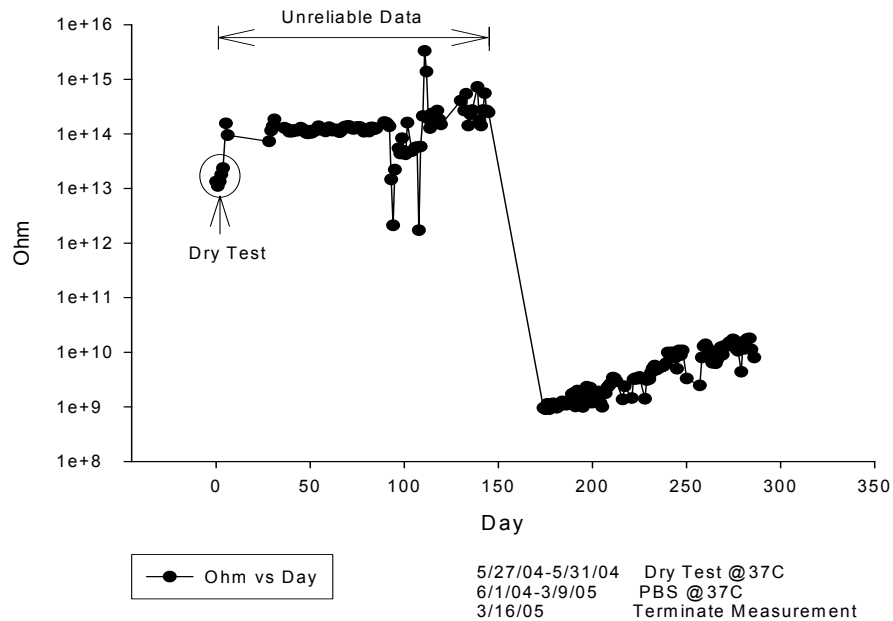




RSHFV3D3TBP041404(E4)
1u film @ condition 2

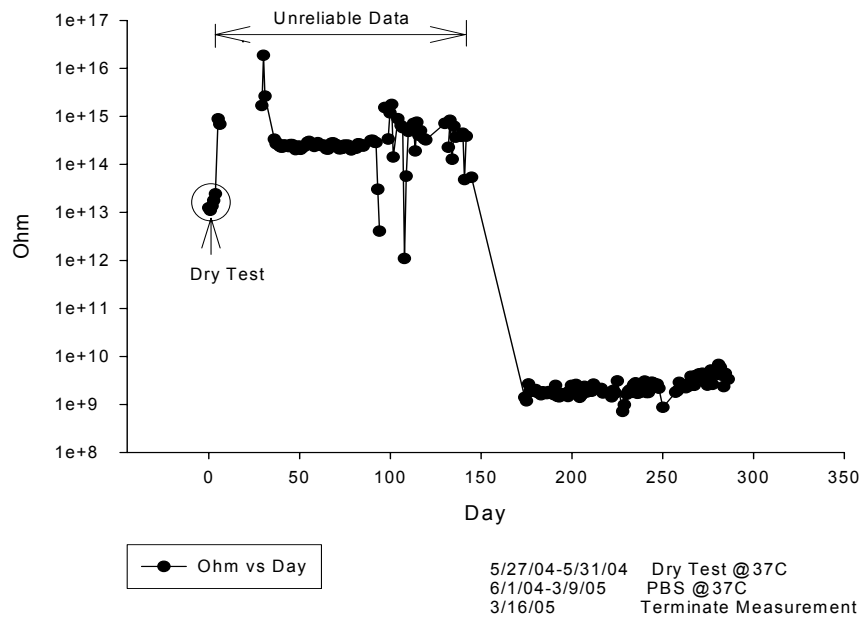


RSHFV3D3TBP041404(E6)
1u film @ condition 2

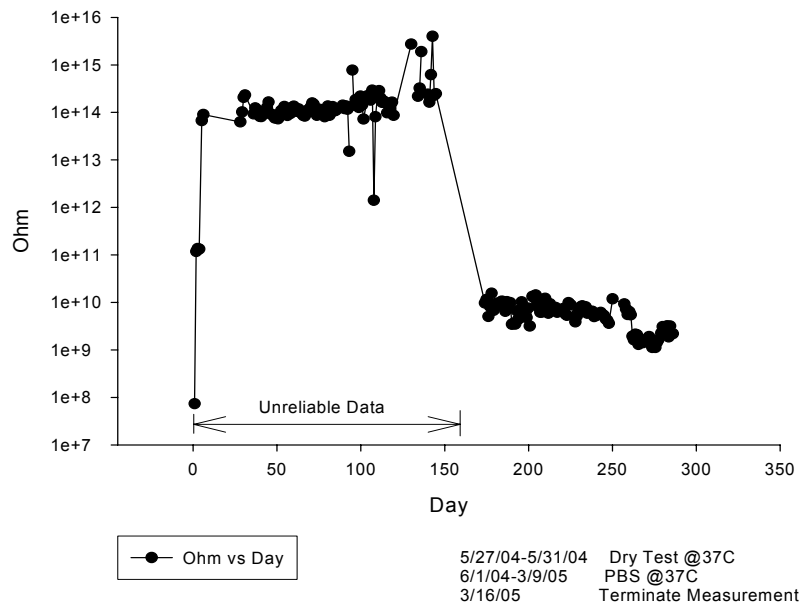




RSHFV3D3TBP041404(E8)
1u film @ condition 2



RSHFV3D3TBP041404(E10)
1u film @ condition 2





Solder Joining

A low temperature soldering method would be quite useful, particularly for polymer substrates. The electrically conductive nickel filled epoxy has been recommended for use where exposure to salt water causes silver based systems to corrode. Three Ni based epoxies have been studied in this experiment. The first one is 10HTN from Master Bond Inc. featuring high performance properties such as high shear, high peel strength, and relatively low resistance. The second system N30 is from EPOXY Technology. The last Ni epoxy EMCAST531-1 supplied by Electronic Materials Inc is originally designed for automotive under hood use. Although these one component high purity nickel conductive systems require no mixing, the thick paste makes the processing a little more challenging. All systems are formulated to cure at elevated temperatures. Nine test devices (RSNi10HTNA,B,C,D & RSNiEPOXYN30A,B,C & RSNiEMCAST531-1A,B) were assembled as follows.

A) Cut 4 pieces 0.5"x0.5" Si wafer for Ni10HTN.

Prepare 3 pieces pre-cut 0.5" Dia. Si wafer for NiEPOXYN30.

Prepare 2 pieces pre-cut 0.5" Dia. Si wafer for RSNiEMCAST531-1.

Prepare 9 pairs of 1foot long silicone insulated wires (Baywire) from Bay Associates. Clean the wires with soap and rinse with warm water to remove baking soda used as anti-stick agent. Clean the wires further with isopropanol/DI₂H₂O/ isopropanol, 1 minutes each in ultrasonic bath.

B) Scrape Si surface with diamond pencil and etch the surface with 1% HF to remove oxide. For all the samples except RSNi10HTNA,B,C, before HF is wiped off, scrape Au wire onto the Si surfaces under HF drop in order to leave some Au trace and make better contacts.

C) Bond Baywire onto cleaned Si surface with Ni epoxy and cure at 125⁰C, 1 hour for RSNi10HTN & RSNiEPOXYN30, and 15 min for RSNiEMCAST531-1.

D) Repeat steps C) & D) to make contact on the other side of Si wafer.



E) Place the partial assembled samples into a Teflon mold.

For RSNi10HTNA,B & RSNiEPOXYN30A,B,C & RSNiEMCAST531-1A, fill the mold with silicone R2188 from Nusil and vacuum the assembly to remove air bubbles. For RSNi10HTNC,D & RSNiEMCAST531-1B, fill the mold with silicone MED4-4220 from Nusil and with no vacuum. Cure the assembly at 125⁰C for 3 hours. Remove the samples from the mold.

F) Place the samples and Pt reference electrode into a long glass tube for test.

In this experiment, the leakage current measurements were referenced to the external solution Pt electrode to test the effectiveness of silicone encapsulation. Hand measurement of electrical conductivity between the contacts evaluates the effectiveness of Ni epoxy contact to Si substrate. Electrical conductivity measurements are summarized in table 2. Although Baywire is insulated with silicone, it is found that Nusil silicones do not bond Baywire well. Failure often occurred at interface of silicone jacket over Baywire under soak (e.g. RSNi10HTNC/MED4-4220, RSNiEPOXYN30C/R2188, RSNiEMCAST531-1B/MED4-4220). From the pass test data, R2188 seems had better encapsulation in terms of longer test period for the same type of Ni epoxy and this result apparently is due to the fact that R2188 was vacuumed in order to remove air bubble. During vacuum process, silicone spread out and covered much more length of Baywire; therefore, the interface of R2188 and Baywire was often not exposed to saline solution under soak. In this experiment, crack in silicone coating was also observed as another cause of failure, RSNi10HTND cracked in MED4-4220 coating after 10 weeks, and RSNiEPOXYN30A&B cracked in R2188 coating after 9 months and 21.5 months measurement respectively. In conclusion, because MED4-4220 has stronger mechanical properties than R2188, MED4-4220 should be better choice for encapsulation. Moreover, it is known that Nusil silicones bond well to silicone tubing from A-M System or Dow Corning; therefore sliding silicone tubing over Baywire will avoid the problem of poor bonding between Nusil silicones and Baywire. Furthermore, vacuum silicone to remove trapped air bubbles may also help silicone adhesion to contacts as well as to substrates. While so much needs to do for improving silicone encapsulation, it is found that Ni epoxies are not effective in terms of making



good contacts on Si substrate. From limited data, it is found that electrical conductivity for most of the devices increased three orders of magnitude after 14 month test. A more frequent measurement over electrical conductivity should be conducted in the future experiments to evaluate other materials for the contacts.

Table 2. Summary of Electrical Conductivity Measurements for RSNi10HTN,N30,EMCAST531-1

RSNi10HTN				
	RSNi10HTNA/R2188	RSNi10HTNB/R2188	RSNi10HTNC/MED4-4220	RSNi10HTND/MED4-4220
11/6/02	~264 K Ω	~354 K Ω	~31 K Ω	~286 K Ω
1/8/04	~6x10 ⁹ Ω /5V	~1.5x10 ⁸ Ω /5V		
6/28/04	~6x10 ⁹ Ω /5V	~1.1x10 ⁸ Ω /5V		
2/13/06	~1x10 ⁹ Ω /5V	~1.3x10 ⁸ Ω /5V		
RSNiEPOXYN30				
	RSNiEPOXYN30A/R2188	RSNiEPOXYN30B/R2188	RSNiEPOXYN30C/R2188	
10/29/02	~1.9 K Ω	~1.2 K Ω	~1.3 K Ω	
1/8/04	~1.8x10 ⁶ Ω /5V	~1.6x10 ⁶ Ω /5V		
6/28/04	~5.4x10 ⁶ Ω /5V	~4x10 ⁶ Ω /5V		
2/13/06	>10 ⁷ Ω	>1.7x10 ⁷ Ω		
RSNiEMCAST531-1				
	RSNiEMCAST531-1A/R2188	RSNiEMCAST531-1B/MED4-4220		
11/26/02	~1.9 K Ω	~3.2 K Ω		
1/9/04	~28 K Ω /5V			
6/28/04	~1.1x10 ⁵ Ω /5V			
3/30/06	~4.7x10 ⁹ Ω /5V			

Wire Solder Joints

The longevity of solder joints between various wires and solder components was evaluated. Seventeen constructions were made between 4/96 and 2/. Five different wires were used in the evaluation: Platinum, platinum/Iridium, copper, gold and Belden silver plated copper multistrand wire. The solders evaluated were Sn62(a combination



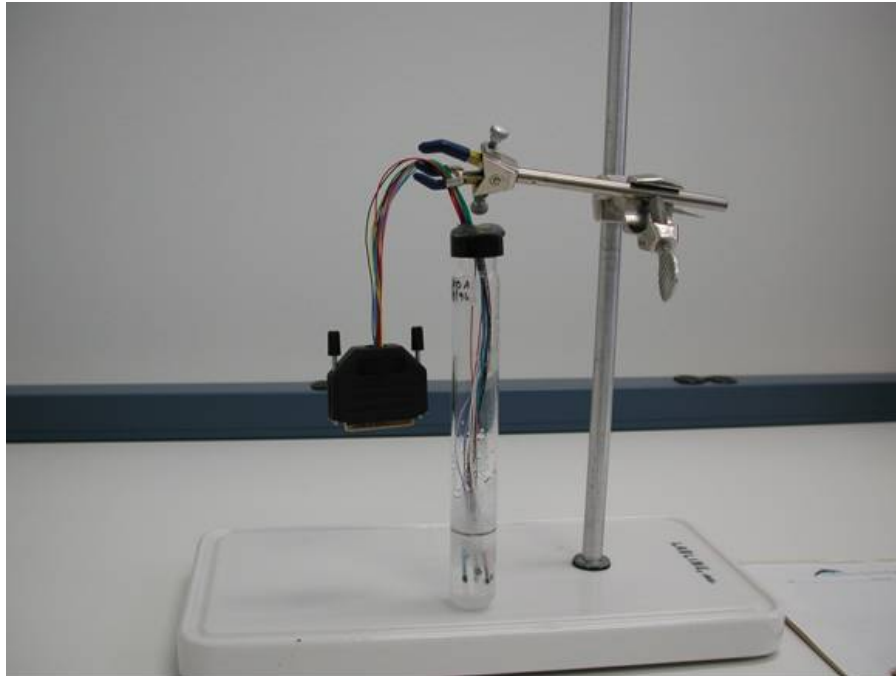
of 62% tin, 38% lead), Sn63(a combination of 63% tin, 37% lead), EpoTek H20E(a two component electrically conductive silver epoxy), Indium(an alloy composed of 90% Indium and 10% silver), silver silicone(Nusil CV-2644, a 2-part nickel/silver silicone mix) and a solder of Sn(98%)-Ag (2%).

The constructions were made as follows:

Six constructions of each wire/solder connection were made. Lengths of the wires in question were cut to extend beyond the length of an 8" long tube. These were flamed, if needed, to remove insulation and soldered together using the solders in question. A section of silicone tubing was threaded over the joint and the tube filled with Nusil CF2-2186 (fast curing silicone). The wires were then threaded through a larger Teflon tube, placed in the glass long tube, and the wire ends threaded through a hole in the top cap and soldered to a 25 pin connector. A reference wire was also placed along with the test wires, threaded through the top and soldered across 2 of the pins. Saline solution with 1% AgNO_3 was added to cover the joint tubes and the long tube was sealed at the cap hole with silicone. The unit was placed in a heat block at 90°C. Measurements were made using a single dedicated multimeter, approximately monthly, recorded and the long tubes refilled as necessary.

Records of the measurements noted the date of measurement, temperature of the heat block and the voltage across the connection. A separate record noted the initial ohms, the date the joint started to fail (an indication that the joint had started to fail would be a reading that showed an approximately 25% change). A final date of fail showed the point at which the unit was not stable in reading. A summary file was kept to show when each of the six constructions failed for each wire sample.

The sample unit as constructed is shown below:



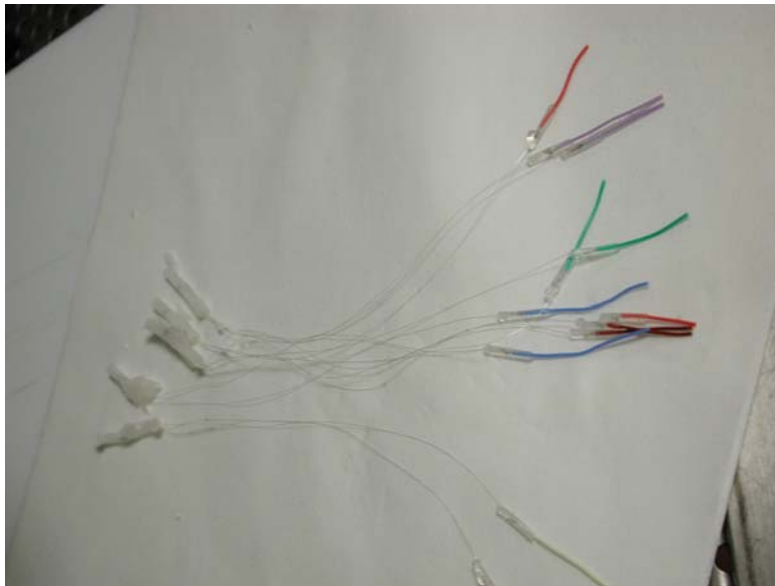
The summary of joint failures is shown in the following table:

Wire	Solder	Failed	Start	Failed	Failed	Failed	Failed	Failed	Failed
Pt	Sn62	0 of 5	5/96						
Pt	Sn63	2 of 4	6/96	1/02	12/05				
Pt	H20E	0 of 6	6/96						
Pt	Sn98%-	0 of 3	2/97						
Ptlr	Sn62	6 of 6	6/96	12/96	2/98	2/98	10/98	12/99	1/02
Ptlr	Sn63	0 of 6	6/96						
Ptlr	H20E	1 of 6	6/96	6/00					
Ag	Sn62	6 of 6	5/96	11/96	2/98	3/99	6/02	1/04	6/05
Ag	H20E	1 of 6	5/96	6/00					
Ag	In	2 of 6	6/96	12/99	2/05				
Au	H20E	5 of 5	6/96	12/96	2/97	4/97	3/99	3/06	
Au	In	0 of 4	6/96						
Au	silver	6 of 6	7/96	All					
Belden	Sn62	0 of 6	5/96						
Belden	Sn63	0 of 6	5/96						
Belden	H20E	0 of 6	5/96						
Belden	In	6 of 6	5/96	8/96	1/97	8/97	1/01	1/01	4/02

The failure points are clearly shown in this sample (Belden/Indium) noted as LBINDA:



All six constructions of the four completely failed units were cut apart to determine the failure point(s).



LBINDA

The first, LBINDA (Belden/Indium) showed no corrosion along the wires, though the solder was granular, gray and some had a brown stain.



All, but one of the units was so swollen, that the silicone tubing had split.





LAG62A

The construction of Ag wire and Kester solder Sn62 (LAG62A) showed no corrosion of the silver wire in the Teflon insulation, not even tarnish, and the conductivity across the Belden/Ag wires was tested and found to be fine. The solder showed a “crystalline” surface with black cracks.



After removing the silicone tubing, it was evident that the corrosion had occurred on the length of uninsulated wire before the solder joint, the area that had been flamed to remove the Teflon coating prior to soldering. This area, then, had not been covered by the solder joint.





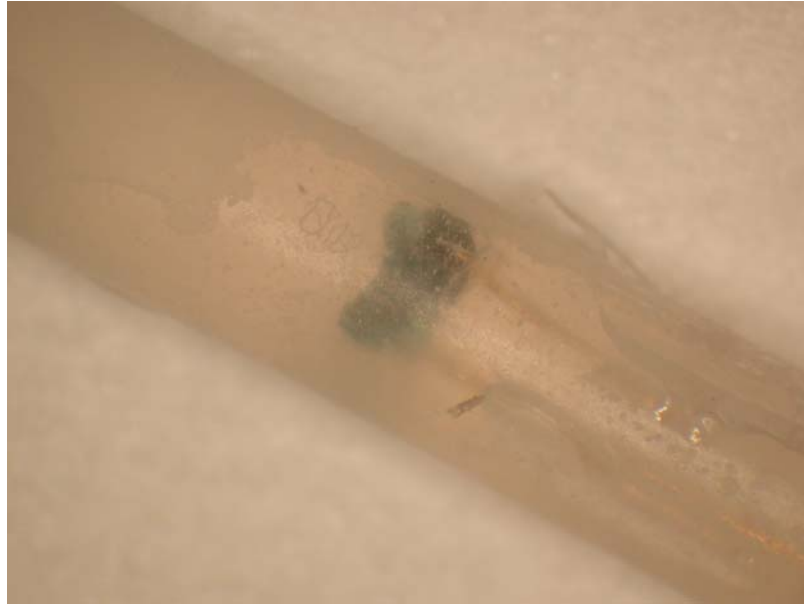
LPI62A

The third construction that totally failed was LPI62A (Platinum/Iridium wire/Kester solder Sn62). In this unit, the solder connections are oxidized to a white color and in some, the solder joint is broken apart.



LAUSSA

The last construction that failed totally is LAUSSA (Au wire/silver silicone). This construction never gave any reasonable readings. All connections were unstable. In this construction the corrosion at the end of the gold wires was green which is odd – prior gold corrosions were distinctively purple.



In the pictures below, discoloration at the gold/Belden join is evident, probably caused by incomplete removal of flux. The joints between the Belden/Silver/Gold joints were verified as conductive and not the failure point.



The silver silicone joints were essentially non-corroded as shown below:





The unstable readings from these silver silicone samples may be explained by the level of silver in the silver silicone more than a failure of any of the joints since they were unreliable from the beginning and showed no corrosion.

All other samples being tested will continue and other samples will be created as the contract allows.



CVD Deposition of Silicones

Work over the past months has focused on three areas:

1. Preparation and submission of a journal article on the synthesis and reaction mechanism of V₃D₃ films
 2. Analysis of the effect of deposition conditions on the electrical properties of the films
 3. Initial literature review to find possible monomers for surface modifiable copolymer
-
1. A full length article detailing the synthesis, molecular structure, and reaction mechanism of the V₃D₃ polymer has been prepared and submitted to Langmuir for publication. Results include:
 - a. FTIR analysis demonstrating reaction of >95% of all vinyl content out of the films and retention of all siloxane ring moieties. This creates a polymer structure that is very crosslinked, making it a more chemically inert, tougher material. The retention of the siloxane ring moieties allows the film to retain flexibility and not become brittle. Figure 6 within the paper shows a schematic of the polymer structure within the deposited films.
 - b. An analysis of polymer chain length (average 8.9 monomer units per backbone segment) based on the XPS spectra of the material.
 - c. An apparent activation energy of 28 kJ/mol for the deposition process with respect to filament temperature, indicating an increase in deposition rate with increasing filament temperature.
 - d. An apparent activation energy of -23.2 kJ/mol for the deposition process with respect to substrate temperature indicating a decrease in deposition rate with an increasing substrate temperature. This is indicative of an adsorption limitation in the deposition process.



A pdf of the submitted manuscript is attached. A final, revised copy will also be submitted once the paper has been accepted.

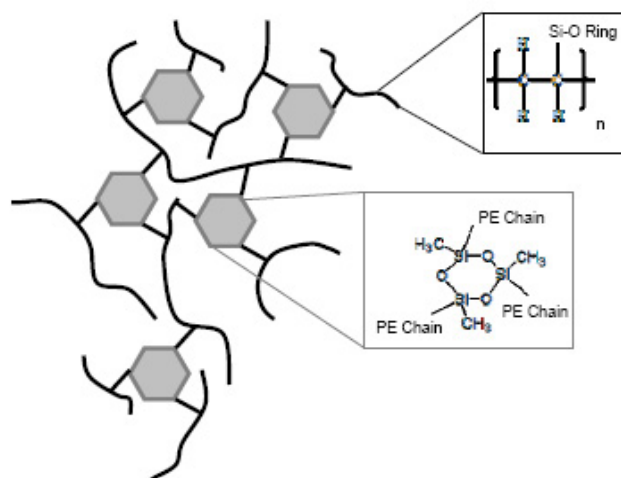


Figure 6. Schematic representation of the matrix structure of the final polymer film. The hexagonal units represent the intact siloxane rings which act as crosslinking moieties for multiple carbon backbone chains.

2. A range of deposition experiments have been performed to assess the variation of the electrical resistivity of the material based on deposition conditions. Resistivities were seen to vary between 10^{13} and $10^{15} \Omega\text{-cm}$. It has been found that film resistivity is independent of deposition pressure below a certain threshold at which the V_3D_3 monomer begins to condense. This pressure value varies with substrate temperature, but films of optimal quality are seen at pressures below 350mTorr. In addition, the resistivity is also seen to be independent of annealing temperature in the range between 200-325°C. However, some dependence of film resistivity on substrate temperature was observed. Further experiments will be performed to try and quantify this dependence in order to optimize film growth rate without negatively impacting polymer electrical properties.



3. An initial literature review has been performed to find possible co-monomers to utilize with V_3D_3 in the creation of a surface modifiable polymer. The goal would be to deposit a bulk film of pure V_3D_3 polymer which could then be graded into a copolymer very near (50-100nm) its surface. This would provide optimal bulk electrical properties while allowing for attachment of bioactive peptides to improve implant stability. A number of acrylate and methacrylate compounds have been identified and will be evaluated over the coming months.